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ERRATA

<u>Page</u>	<u>Line</u>	<u>From</u>	<u>To</u>
1	1	Phenomena	Phenomenon
11	19	T_2 to T_2	T_2 to T_1
19	6	varies	vary
28	15	existed	exited
29	15	Glyptol	Glyptal
31	17	Glyptol	Glyptal
33	5	Cathotometer	Cathatometer
33	5	Brown Electron Recorder	Brown Elektronik Recorder
37	3	Tabilang	Tagliabus
38	10	Research	Refining
46	9	is	are
67	6 and 7	d_p	d_p
71	8	$\frac{a^4}{a^5}$	$\frac{a^4}{a^5}$
72	8	$\frac{a^5}{150}$	$\frac{a^5}{120}$

FINAL REPORT
1965

PHYSIO-CHEMICAL FACTORS CONTRIBUTING TO THERMOELECTRIC PHENOMENA

PART 1: THOMSON HEAT IN METALLIC SYSTEMS

by

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O.N.R.
669(15)

S.U.R.I. Report No. 969-665F

Date: June, 1965

BRIEF

In the final report to the Office of Naval Research, on the Nonr-669(15) program at Syracuse University, is enclosed one complete doctoral dissertation on the Thomson heat in Metallic Systems. Since this work comprised a major effort for the past three years at Syracuse, it is included in its entirety. The theoretical study and experimental data from the Thomson heat dissertation is to be presented to the open literature as a publication within the following year.

ABSTRACT

The fundamental concepts of the Thomson heat and the basic equations governing the heat flows associated with its generation are presented. From considerations of these equations, two new techniques for measuring the Thomson coefficient have been developed and examined experimentally. The two new techniques of studying a sample subjected to thermal and electrical gradients, included a non-equilibrium approach, in which the initial rate of change of temperature within the sample leads to a value of the Thomson coefficient, and a method based on equilibrium considerations. The latter leads to a very simple, straightforward equation relating the Thomson coefficient to the change in equilibrium temperature associated with a reversal of current flow.

An experimental apparatus was designed and utilized to examine the validity of the equations which were developed. The two techniques, as well as a standard direct measurement technique, which involved a change in current to compensate for the temperature change resulting from a reversal of Thomson heat, have been applied to measurements of the Thomson heat of nickel and lead. The measurements were made in the temperature range of 40°C, where very little, if any, reliable data is available. The results obtained with these two new techniques agree reasonably well with the data obtained utilizing the standard technique and data extrapolated into this temperature range from previous work.

TABLE OF CONTENTS

	page
Acknowledgement	ii
List of Tables	iv
List of Illustrations	v
I. Introduction	1
II. Theory	8
III. Other Experimental Work	19
IV. Experimental	27
A. Calorimeter	28
B. Thermocouples	31
C. Electrical Circuit and Controls	35
D. Power Supply	35
E. Thermal Gradient	36
F. Samples	37
G. Experimental Techniques	40
V. Results and Discussion	45
VI. Summary and Recommendations	60
 Appendices	
A - Generation of Heat in a Simple Coil	63
B - Solution of Equilibrium Equation for Determining Thomson coefficient	66
C - List of Symbols	73
Bibliography	76
Biographical Note	79

LIST OF TABLES

Table No.		Page
1A	Values of the Thomson coefficient of lead using Method I	45
1B	Values of the Thomson coefficient of lead using Method I, with different boundary conditions	46
2	Values of the Thomson coefficient of nickel using Method I	49
3	Values of the Thomson coefficient of nickel using Method II - Special Case	56
4	Calculations of the Thomson coefficient from previous data using Method II - Special Case	57

LIST OF ILLUSTRATIONS

Figure No.		Page
1	Apparatus first used to measure Thomson coefficient	23
2	Apparatus used by Lander to measure Thomson coefficient	23
3	Calorimeter for Thomson coefficient determination	29
4	Detailed diagram of end sinks of calorimeter	30
5	Temperature recording system	33
6	Sketch of curves obtained with two directions of current flow in a nickel sample	48
7	Sketch of method for determining Thomson coefficient	51
8	Data obtained on nickel samples using Method III - specific boundary conditions	53
9	Data obtained on nickel samples using Method III - specific boundary conditions	54
10	Comparison of Method II and Method III for calculating the Thomson coefficient	55
11	Approach to equilibrium of a simple heater coil	64
12	Approach to equilibrium of a simple heater coil for different rates of input	64
13	Temperature distribution over a linear base on a nickel rod	69
14	Change in slope with position in a nickel rod	70

I. INTRODUCTION

The phenomena of thermoelectricity encompasses those processes in which there is generation of electrical currents by means of imposed thermal gradients or the creation of reversible heat by means of electric current flow. The practical applications of these phenomena, such as in the cases of thermal refrigeration and the generation of electrical power from heat, has prompted a great deal of research in the last decade in the hope of optimizing various thermoelectric devices. Theoretical considerations of the results obtained from these and more fundamental investigations have revealed a rather complex interaction between conduction electrons and thermal currents, i.e. electrons and phonons (1).

The purpose of this investigation is to present a fundamental analysis of the factors involved in the generation of the Thomson heat. This purpose can be subdivided into two major considerations:

1. Complete development of the various heat and electric flow equations governing the evolution of heat, and
2. Presentation of two essentially new techniques for measuring the Thomson coefficient, based on these fundamental equations.

With the application of a temperature gradient to a conductor, in the absence of an electric field, not only will the gradient generate a flow of heat, but also an actual electric current. In order to observe this current, however, it is necessary to form a complete circuit consisting of two dissimilar metals, as the symmetry of a monometallic

system annihilates any current which is produced. The electric current developed in the circuit by the thermal gradient will depend upon the resistance of the wires making up the system. Alternately one could avoid the need of considering the resistance of the wire by observing the potential developed across the terminals. In this way the observed potential would be a function only of the thermal gradient and the particular materials making up the couple. The generation of this thermoelectric potential is known as the Seebeck effect, in honor of the man to whom the discovery is attributed (2). Of the three common thermoelectric effects, it is probably the most familiar and widely used. A term often employed in thermoelectric calculations is the thermoelectric power (S), which is simply the derivative of the seebeck potential (V) with respect to temperature, i.e. dV/dT .

The second thermoelectric effect to be discovered was the Peltier heat (π), which is the heat developed in a reversible manner at a junction of two dissimilar metals when an electric current is passed from one substance to the other (3). The heat generated at such a junction should not be confused with the irreversible Joule heat, which is always evolved from a conductor carrying an electric current. The Peltier heat is associated with the transfer of charge from the interior of one substance to the interior of the second, and is not, as sometimes asserted, in any way related to surface charges.

William Thomson (4) proposed the existence of a third thermoelectric effect on obtaining erroneous results in applying the laws of thermodynamics to the first two effects. Thomson postulated that if an electric

current is passing through an individual conductor under an imposed temperature gradient, then there should be a reversible heat developed per second, over and above the irreversible Joule heat. This additional, or Thomson, heat is a function of the electric current, temperature gradient and the Thomson coefficient (τ), which is a bulk parameter of the conductor, the same as resistivity and specific heat.

Thomson also derived (5) the following relationships, often called the "Kelvin relations", between the three common thermoelectric parameters:

$$\tau = T \frac{dS}{dT} \quad (1)$$

$$\pi = TS$$

$$\text{where } S = dV/dT$$

These relations were first developed by adding the irreversible Joule heat to the reversible Thomson and Peltier heats. The addition of reversible and irreversible heats is contrary to general thermodynamic considerations (6), and, therefore, these equations were not very satisfactory from a theoretical point of view. A great deal of effort by leading theoreticians (6,7) has been made to place these equations on a sound theoretical basis; however, there has not as yet been a completely satisfactory development of these relations, with the possible exception of irreversible thermodynamic concepts, where the equations have been developed with a minimum number of assumptions (8,9,10). There can be no doubt, however, of the validity of these equations, since they have been substantiated time and again by experimental investigations.

Although the Kelvin relations appear to offer the simplest experimental approach for determination of the various thermoelectric parameters, i.e. through measurement of the thermoelectric power, a careful analysis of the Thomson coefficient data suggests that a more direct method, which did not involve the differentiation of a curve, should be developed. For example, a number of isothermal Thomson coefficient versus composition curves prepared from the differentiation of Seebeck data, presented by Salkovitz (11,12) and Rudnitskii (13), indicated that τ varied as a function of composition in the single phase region; however, on crossing into the two phase region, τ often became quite erratic with changing composition. If τ varies as function of composition, as demonstrated in a single phase solid solution, then in a two phase region in which the composition of the phases are constant, and only the macro-volumes are changing, one might expect the variation of τ with composition to behave somewhat as Vegard's law behaves at a single phase - two phase boundary. That is, variation to the boundary in the single phase region and nearly constant τ in the two phase region. Such a discontinuity is not evidenced from the calculations of τ from the Seebeck data. In making measurements in regions such as this, or in any area where τ would be expected to change rapidly, calculations based on the Kelvin relations could be subject to error, since it is very difficult to make precise slope measurements on rapidly changing curves, i.e. dS/dT (cf. Equation 1).

A simple, but fairly reasonable, model of the Thomson heat may be developed from the atomic scale, if one assumes the free electron model

of a solid to be an adequate first approximation. In such a model, where no interaction between the electrons and the lattice is assumed, the thermoelectric current can all be attributed to the diffusion of the electrons from the hot end of the conductor to the cold end, with a consequent release or absorption of heat. Such a view has led to the common terminology of calling the Thomson coefficient the "specific heat" of electricity (14), since it expresses the quantity of heat absorbed or evolved per unit of electric current in passing through the sample. Theoretical calculations of the Thomson coefficient based on this consideration and employing Fermi-Dirac statistics, has led to surprisingly close agreement with experimental data for a number of the simpler metals (15), e.g. the alkali metals.

The idealized free electron model is approached by a few real metals; however, there are few cases, if any, where there is absolutely no interaction between the free electrons and the lattice. This being the case, one would expect the thermal energy flowing down the temperature gradient, in the form of lattice waves (phonons), to have some effect on the electric current in the system. This has been found to be true in some metals in specific temperature ranges. The streaming phonons are believed to have a tendency to sweep, or drag, the electrons from the hotter to the colder end of the conductor. The effect is commonly called the "phonon-drag effect" and as would be expected, it is dependent upon the degree of interaction between the lattice and the electrons. If there is an interchange of heat between the electrons and the lattice, the "phonon-drag effect" must be related

to the ability of the lattice to absorb heat, i.e. the lattice specific heat, as illustrated in the following equation for the contribution of "phonon-drag" to the Thomson coefficient (16):

$$\tau = \frac{c_g}{\beta e} \alpha \quad (2)$$

c_g = lattice specific heat per atom

α = probability of phonon-electron collision, as compared to other collisions, i.e. phonon-phonon, phonon-impurity

β = number of conduction electrons per atom

As the temperature approaches absolute zero, the phonon-electron collisions become dominant over other types of phonon interactions, causing α to approach a maximum of one. On the other hand, the lattice specific heat is known to decrease as T^3 as absolute zero is approached. At relatively high temperatures phonon-phonon interactions become dominant, causing α to approach zero. Combining the effects of the decay of α at high temperatures and the decay of c_g at low temperatures, one would expect the magnitude of the phonon-drag contribution to reach a maximum at intermediate temperatures, decaying on either side. This was substantiated (17) experimentally at temperatures between 10 and 50°K, where thermoelectric powers of as high as several millivolts per degree have been observed. In the metal systems investigated to date, the phonon-drag contribution to the Thomson heat becomes negligible in the vicinity of room temperature.

As in the case with electrical properties, the thermoelectric effects are influenced by the presence of impurity atoms in the lattice.

When the electrons tend to diffuse from one end of the sample to the other, they will be scattered in route by impurity atoms. If the scattering cross section is the same for electrons with the higher energy moving from the hot end as that for electrons with lower energy from the cold end, then the impurities would tend to have no net effect on the thermoelectric properties. As would be expected, however, the scattering cross section of an impurity atom is a function of the energy of the electron; thus one finds that the scattering cross section, A , would decrease, or the mean free path, l , would increase, with increasing electron energy. If impurities are present in a sample the thermoelectric equations must be modified to take into account the variation of cross section with electron energy. The effect of impurity atoms has been studied at low temperatures (18) where the behavior was found to follow an equation of the form:

$$S = \frac{2c_{el}}{3e} \left(1 - \frac{d \ln A(E)}{d \ln E} \right)_{\epsilon_0} \quad (3)$$

where

- c_{el} = electron specific heat
- $A(E)$ = the energy dependent scattering cross section
- e = charge on the electron
- E = electron energy

and the derivatives are evaluated at the Fermi level (ϵ_0^F). The experimental data agrees reasonably well with this equation at very low temperatures where other processes are not dominant.

II. THEORY

Since the proposal of the Kelvin relations, the theoretical analysis of the thermoelectric properties of materials has been presented from two different standpoints; irreversible thermodynamics as rigorously discussed by Onsager (9,19), de Groot (10), Denbigh (20) and Prigogine (21), or from the kinetic theory of electrons through Boltzman's equation, as discussed by Wilson (22) and Ziman (1), to name only a few. Since both of these approaches lend a degree of understanding to the Thomson coefficient and its relations to metals and alloys, a brief resume of each is presented.

A. Irreversible Thermodynamics

In the irreversible thermodynamic treatment, the creation and transport of entropy plays a significant role. The irreversible thermodynamic postulates, as reviewed by Leech (23), can be introduced in the form of an equation linking the entropy flow (J^S) and the entropy density (S_D) by means of the balance equation:

$$\frac{\partial S_D}{\partial t} = - \nabla \cdot J^S + \frac{1}{T} \sum_i J_i X_i \quad (4)$$

where

J_i = electric and heat current flow vectors

X_i = thermodynamic "forces" giving rise to currents

It is further assumed that at or near equilibrium:

$$J_i = \sum_j L_{ij} X_j \quad (5)$$

is valid, and that the Onsager relations hold:

$$L_{ij} = L_{ji} \quad (6)$$

In rigorous treatments, these are deduced from fundamental postulates. Although there is considerable choice in the form of the flow vectors J_i or the appropriate conjugate quantities X_i , once chosen the arbitrariness is removed.

The phenomenological equations relating entropy flow density J_s and particle current density J_e , are then related according to Domenicali (24) by:

$$J_e = -L_{ee} \nabla \bar{\mu} - L_{es} \nabla T \quad (7)$$

$$J_s = -L_{es} \nabla \bar{\mu} - L_{ss} \nabla T$$

where $L_{es} = L_{se}$, in accordance with Equation (6). However, a new set of phenomenological equations are necessary to define heat flow J_q in terms of J_e and J_s . Following Callen's (25) work, Domenicali arrived at:

$$J_e = -M_{ee} \nabla \bar{\mu} - \left(\frac{1}{T}\right) (M_{eq} - \mu M_{ee}) \nabla T \quad (8)$$

$$J_q = -M_{eq} \nabla \bar{\mu} - \left(\frac{1}{T}\right) (M_{qq} - \mu M_{eq}) \nabla T$$

where the \underline{M} and \underline{L} coefficients are related by

$$L_{ee} = M_{ee}$$

$$TL_{es} = M_{eq} - \mu M_{ee}$$

$$T^2 L_{ss} = M_q - 2\mu M_{eq} + \mu^2 M_{ee}$$

$$\mu = \text{chemical potential}$$

$$\bar{\mu} = \text{electrochemical potential}$$

If one considers the steady electronic current J_e , particles/sec-area, in a cylindrical rod, with no temperature gradient, then the ratio of Equations 7A : 7B reduces to:

$$\left(\frac{J_s}{J_e}\right)_{\nabla T=0} = \frac{L_{es}}{L_{ee}} \equiv S^* \quad (9)$$

which defines the "transport entropy per particle". The ratio of Equations 8A : 8B yields:

$$\left(\frac{J_q}{J_e}\right)_{\nabla T=0} = \frac{M_{eq}}{M_{ee}} \equiv Q^* \quad (10)$$

which defines the "transport heat per particle". It can be further shown that $L_{ee} = \sigma/e^2$, where σ is the isothermal conductivity.

These terms, developed from fundamental concepts, can be directly applied in the determination of the values of the various thermoelectric coefficients. Values of the Thomson coefficient, for example, can be determined by applying these concepts to the equation developed to calculate the additional rate of heat flux

required to maintain a given temperature distribution once the electrical current is turned off. The solution takes the form:

$$e\Delta E = - \int_V \left(T \frac{\partial S^*}{\partial T} \right) \vec{J} \cdot \nabla T dV - e \int_V \left(\frac{1}{\sigma} \right) J^2 dV \quad (11)$$

where

$$\tau = - \left(\frac{1}{e} \right) T \frac{\partial S^*}{\partial T} = \text{Thomson Coefficient}$$

$$J = \text{electrical current density} \equiv - e J_e$$

ΔE = the rate of heat transferred into volume element \underline{v} to maintain temperature gradient

In order to determine τ , it is necessary to remove it from under the integral sign, which can most easily be accomplished by considering a long homogeneous section of thin wire. In the steady state situation, Equation (11), then reduces to the experimentally usable relation:

$$\Delta E = I^2 R \pm I \tau \Delta T \quad (12)$$

The reversible Thomson heat ($\tau I \Delta T$) adds or subtracts to the irreversible Joule heat ($I^2 R$), depending upon the direction of electric current flow with respect to the temperature gradient. The sign convention followed in this investigation is that established by MacDonald (17), in which the positive sign indicates the electrical current is flowing down the thermal gradient, i.e. from T_2 to T_1 where $T_2 > T_1$, and the negative sign indicates the electrical current is flowing up the thermal gradient.

Equation (12) gives a very satisfactory derivation from fundamental considerations in the steady state, which can be used in

direct measurements.

B. Kinetic Theory

The kinetic theory approach to transport properties in solids is introduced through the assumption that the electron distribution in the free electron gas may be represented by an equation developed by Ziman (1), which is of the form:

$$du = f(v_x, v_y, v_z ; x, y, z ; t) dv_x dv_y dv_z dx dy dz \quad (13)$$

where du is the number of electrons at time t in the volume element dx, dy, dz , with velocities between v_x and $(v_x + dv_x)$. Accepting the most elementary case and allowing Equation (13) to define "f", the distribution function of the electrons, then:

$$\iiint_{-\infty}^{+\infty} f dv_x dv_y dv_z = N(x, y, z ; t) \quad (14)$$

where N is the density of free electrons at time t . The distribution function, f , has the equilibrium value, f_0 , in an isothermal conductor rod, not under the influence of electric or magnetic fields, and is given by the Fermi-Dirac function:

$$f_0 = 2 \left(\frac{m}{h}\right)^3 (e^{E - \epsilon^* / kT} + 1)^{-1} \quad (15)$$

in which E is the energy of an electron with velocity v_x, v_y, v_z (often presented as k vectors), and ϵ^* is the chemical potential of the electrons.

The Boltzmann equation is presented formally as:

$$- \left(\frac{df}{dt}\right)_{\text{fields}} = \left(\frac{df}{dt}\right)_{\text{collisions}} \quad (16)$$

where the left hand side represents the effect of external fields on the electron without interference, and the right hand side represents the effects of electron collisions on the distribution function.

For the simplest case where the electron flow is due to an electric field and a temperature gradient dT/dx , and all collisions tend to restore equilibrium at a linear rate of restoration, which is proportional to the departure from f_0 , Equation (16) may then be written:

$$\frac{\partial f_0}{\partial v_x} \frac{eE}{m} + \frac{\partial f_0}{\partial T} \frac{dT}{dv} v_x = - \frac{f - f_0}{\tau'(\epsilon)} \quad (17)$$

where it is assumed that $\tau'(\epsilon)$ is the constant restoration rate, irrespective of the type of deviation from equilibrium. The assumptions leading to the restoration rate are approximately true only at high temperatures, $T > \theta_D$, or when scattering is due to impurity atoms.

Utilizing these assumptions, Leach (23) derives a set of phenomenological equations based on kinetic theory which are similar to the irreversible thermodynamic phenomenological Equations (7) and (8):

$$J_x = \frac{Ne^2 \tau'(\epsilon)}{m} E_x - e \tau'(\epsilon) \frac{\partial}{\partial T} \int v_x^2 f_0 d^3v \frac{dT}{dx} \quad (18)$$

$$Q_x = - \frac{e \tau'(\epsilon)}{2} \int v_x v^2 \frac{\partial f_0}{\partial v_x} d^3v E_x - \frac{m \tau'(\epsilon)}{2} \int v_x v^2 f_0 d^3v \frac{dT}{dx} \quad (19)$$

where

$$N = \int f d^3v = \text{electron density}$$

Relating these equations to those developed from irreversible thermodynamics, Leech redefined the Thomson coefficient in terms of the kinetic theory as:

$$\tau = T \frac{\partial}{\partial T} \left(\frac{2}{3} \frac{C_{el}}{e} - \frac{\partial g}{\partial T} \right) \quad (20)$$

where:

C_{el} = electronic heat capacity

g = chemical potential/unit conduction charge

For metallic conductors, g is the Fermi energy per electron per electron charge, and if the following free electron model relations hold:

$$\epsilon^* = \epsilon_0^* - \frac{\pi k T^2}{12 \epsilon_0^*} \quad (21)$$

where

$$\epsilon_0^* = \frac{h^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3} = \text{Fermi level at } 0^\circ\text{K}$$

and

$$C_{el}^{T=0} = \pi^2 k^2 T / 2 \epsilon_0^* = \text{electronic heat capacity}$$

then the Thomson coefficient is related directly to the electron heat capacity per electron:

$$\tau = \frac{C_{el}}{e} \quad (22)$$

which was originally suggested by Thomson.

C. Heat Balance Equations

The equations developed in the previous sections establish a means of determining the Thomson coefficient from first principles. The resulting equations, however, are derived from equilibrium considerations in a specific conductor; and as such, do not give a complete analysis of all the heats involved in the system.

The general equation which is employed for problems which involve heat flows into, and out of a system is:

$$\dot{Q}_I = \dot{Q}_A + \dot{Q}_L \quad (23)$$

where:

\dot{Q}_I = rate of heat input to the system

\dot{Q}_A = rate of heat absorbed by the sample

\dot{Q}_L = rate of heat leaving a unit volume.

One should note that these are rate of heat transport, and not, as often stated, bulk quantities of heat. To gain a complete understanding of the phenomena taking place within a metal rod subjected to the various energy flows, it is necessary to understand how a given rate of heat input can give rise to one equilibrium temperature and a different rate of input, give rise to a different equilibrium temperature. This is briefly described in Appendix A.

Seitz (26) has given a detailed study of the Thomson coefficient using Equation (23) in the form:

$$\frac{dH}{dt} = I \frac{E}{x} - \frac{\partial C}{\partial x} \quad (24)$$

Where dH/dt is the rate at which heat accumulates in a unit volume of conductor carrying both electrical and thermal currents. The term $(I_x E_x)$ in this equation is related to the electrical work done, and the term $(\frac{\partial C}{\partial x})$ is related to the rate of heat flowing out of a unit volume. The equation can be written in a more familiar form by writing E_x and C_x as

$$E_x = -\frac{3}{2} \sqrt{\frac{m}{2}} \frac{1}{K_1} I_x - \frac{T}{e} \frac{d}{dT} \left(\frac{\epsilon^*}{T} \right) \frac{dT}{dx} - \frac{K_2}{K_1} \frac{1}{T\epsilon} \frac{dT}{dx} \quad (25)$$

$$C_x = -\frac{K_2}{K_1} \frac{1}{e} I_x + \frac{1}{3} \sqrt{\frac{2}{m}} \left(\frac{K_1 K_2 - K_2^2}{TK_1} \right) \frac{dT}{dx} \quad (26)$$

where:

$$K_1 = \frac{3}{2} \frac{n_0}{\epsilon_0} \int_0^\infty \epsilon^{\frac{1}{2}} \epsilon \frac{df}{d\epsilon} d\epsilon$$

n_0 = number of electrons per unit volume

ϵ_0^* = energy of Fermi electrons at $0^\circ K$

l = mean free path of electrons

f = distribution function

substituting Equations (25), (26) into Equation (24), one obtains

$$dH/dt = I_x^2 \rho + \frac{I_x}{e} T \frac{d}{dx} \left(\frac{K_2}{TK_1} - \frac{\epsilon^*}{T} \right) + \frac{d}{dx} \left(\kappa \frac{dT}{dx} \right) \quad (27)$$

The first term to the right of the equality in Equation (27) represents the Joule heat, and the third is due to that arising from the conduction of heat in the material. Both of these terms are independent of the relative direction of the electric and

thermal currents, while the second term represents a rate of accumulation of heat, dependent upon the relative direction of the two flows.

Rewriting the second term of Equation (27), heat will be produced at a rate:

$$\left(\frac{dH}{dt}\right)_\tau = \left[\frac{T}{e} \frac{d}{dT} \left(\frac{K_2}{TK_1} - \frac{\epsilon^*}{T} \right) \right] I \frac{dT}{dx} \quad (28)$$

which can now be recognized as the Thomson heat, where the negative of the bracketed term, namely

$$- \frac{T}{e} \frac{d}{dT} \left(\frac{K_2}{TK_1} - \frac{\epsilon^*}{T} \right) = \tau$$

is equivalent to the Thomson coefficient. This equation can be further refined leading to Equation (29):

$$\tau = - \frac{k^2 T}{e} \frac{T^2}{3} \left[\frac{1}{\epsilon_0^*} + \frac{l'(\epsilon_0^*)}{l(\epsilon_0^*)} \right] \quad (29)$$

where the quantity $l'(\epsilon_0^*)/l(\epsilon_0^*)$ can be roughly evaluated using a theory of the mean free path.

Simplifying the nomenclature, Equation (27) can be rewritten:

$$\frac{dH}{dt} = I^2 \rho \pm I\tau \frac{dT}{dx} + k \frac{d^2 T}{dx^2} \quad (30)$$

Under steady state conditions, i.e. $dH/dt = 0$, this becomes

$$- k \frac{d^2 T}{dx^2} = I^2 \rho \pm I\tau \frac{dT}{dx} \quad (31)$$

This differential equation is solved in Appendix B. The resulting expressions are then used in a direct determination of the Thomson coefficient, for both general and special cases.

III. OTHER EXPERIMENTAL WORK

The method most commonly used for the direct measurement of the Thomson coefficient is based on a method perfected by LeRoux (27), and used with slight modifications by Berg (28), Nettleton (29), Young (30), Smith (31), Borelius (32), and Nystrom (33). The actual experimental arrangements used to establish the temperature gradient and design of the apparatus varies slightly from one investigation to another, the main differences lying in the means of detecting the temperature changes and gradients in the sample.

According to Nystrom (33), on subjecting a homogeneous sample to a constant thermal gradient and electrical current, the governing equation can be written:

$$\text{heat produced} = J^2 \rho + J\tau \frac{dT}{dx} \quad (32)$$

If the direction of current is reversed, the first term denoting Joule heat will not change, but the second, denoting the Thomson heat, will change sign. If the current strength is altered by a suitable amount, ΔJ , in connection with its commutation, the total effect will be unaltered. By equating the two equations, one can calculate τ .

The mathematical development of the foregoing begins with the current flow in a direction with respect to the thermal gradient such that the Thomson heat is added to the Joule heat, i.e.

$$J^2 \rho + J\tau \frac{dT}{dx}$$

then, with a reversal and subsequent change of current, one can return

to the original equilibrium, i.e.:

$$J^2\rho + J\tau \frac{dT}{dx} = (J + \Delta J)^2\rho - (J + \Delta J)\tau \frac{dT}{dx} \quad (33)$$

expanding and rearranging:

$$2\tau J \frac{dT}{dx} + \Delta J\tau \frac{dT}{dx} = 2J\Delta J\rho + \Delta J^2\rho \quad (34)$$

and

$$\tau = \frac{\rho\Delta J}{dT/dx} \quad (35)$$

Thus, τ can be calculated directly from the experimental conditions.

Early experiments employed a bolometer coil to detect the temperatures of the sample. In this method a copper resistance thermometer coil was wound around the test specimen as shown in Figure 1, and the change in resistance is detected by a very sensitive bridge circuit. Since the variation of resistance of copper with temperature is known quite accurately, the temperature of the sample at the region in question is readily determined. At thermal equilibrium, as detected by the bolometer coil, the current was reversed and then varied until the temperature of the sample was identical to that established with the original current flow.

More recent investigations (13), have used a similar analysis, only employing thermocouples as the sensing elements. The thermocouples were either taped directly to the side of the specimen or inserted into small surface holes drilled into the specimen.

Nystrom (33) has used a microthermopile to measure both the temperature gradient and the temperature changes associated with reversal

of current flow. The projector and the thermopile were built such that the entire "microscope" could be moved to obtain a maximum emf out of the projected image of the sample. The output of the thermopile was measured with a very accurate potentiometer. Again the procedure for obtaining the Thomson coefficient was the same as that described previously.

This basic technique is quite valid and has provided a great deal of basic data on the Thomson coefficient. Analyses have been made, however, in which Equation (32) has been referred to as a certain amount of heat, which causes a change in temperature of the conductor. Technically, this is incorrect, since it is not a quantity of heat at all, but the rate of heat input to the entire system, none of which is absorbed by the conductor at equilibrium, which although not frequently mentioned, is the actual case considered in this type of analysis. If one does carry out this technique it is also found that dT/dx is not simply the difference in temperature between the end sinks divided by the length of the sample, as is often inferred, but varies throughout the sample and also changes value with reversal of current. The only position at which dT/dx , for current flow in one direction, is the same as that for current flow in the opposite, is exactly at the midpoint of the sample. A complete analysis of this system is given in Appendix B.

In general then, this technique is quite valid for obtaining values of the Thomson coefficient. Some of the current literature (13,33), however, gives an incomplete development of the theory governing the analysis, which can make it quite difficult to obtain a basic understanding of the factors involved in calculating the Thomson coefficient.

Lander (34) has used a rather unique approach for a direct measurement of the Thomson coefficient. He assumed that the conduction heat out of the end of a wire, ignoring radiation losses, is equal to the Joule heat plus the Thomson heat developed between that end and the surface of maximum temperature. A sketch of his apparatus is shown in Figure 2. The two ends of the sample are maintained at the same temperature and the center of the sample is heated electrically. It will be noted that with an electrical current flow (I) in one given direction, the current flow in one-half of the sample will be in the same direction as the thermal gradient and in the other half, against the gradient.

In the absence of Thomson heat the conduction heats flowing out the ends of an isotropic wire are equal if these ends are at the same temperature. Consider a wire with both ends held at absolute temperature T_0 and heated electrically to a maximum temperature T^* . Let the electrical potential at any point be indicated by ϕ and the potential at the two ends be 0 and E. The heat flowing per second through the surface with 0 potential and temperature T_0 is, in the steady state:

$$Q_1 = \phi^* I + I \int_{T_0}^{T^*} \tau dT \quad (36)$$

where ϕ^* is the potential at T^* and I is the electrical current flowing through the wire. Through the surface at potential E and temperature T_0 the heat flowing per second is:

$$Q_2 = (E - \phi^*) I - I \int_{T_0}^{T^*} \tau dT \quad (37)$$

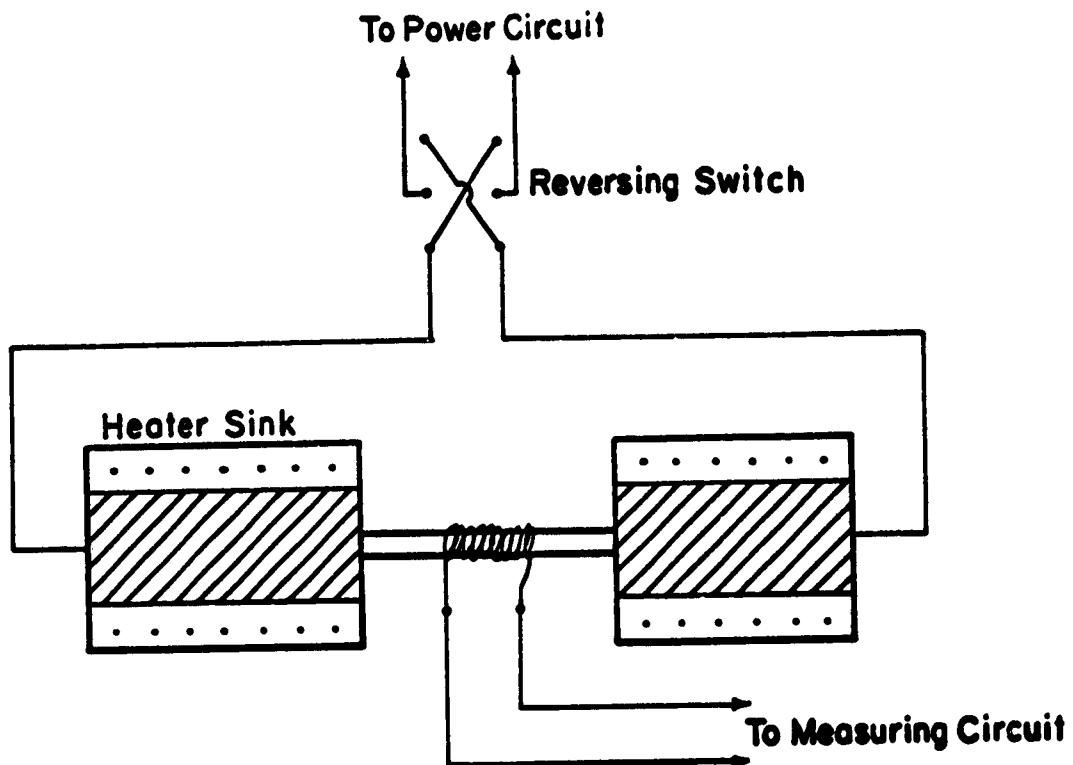


FIGURE 1 - Apparatus first used to measure Thomson Coefficient

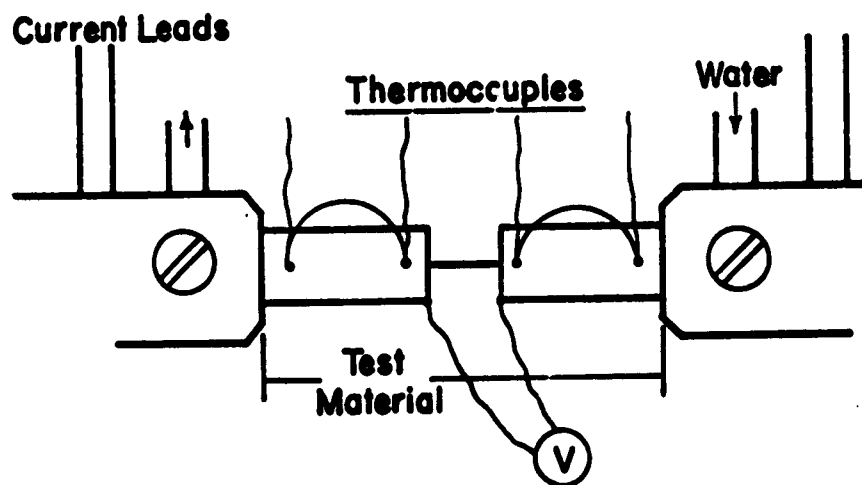


FIGURE 2 - Apparatus used by Lander to measure Thomson Coefficient

The difference between these divided by the total heat output is

$$\frac{(Q_1 - Q_2)}{(Q_1 + Q_2)} = \frac{\Delta Q}{Q} = \left| \frac{(2\phi^* - E)}{E} \right| + \left(\frac{2}{E} \right) \int_{T_0}^{T^*} \tau dT \quad (38)$$

Through mathematical considerations and certain simplifying assumptions this equation finally reduces to:

$$\left(\frac{\Delta Q}{Q} \right) \left(\frac{E}{2} \right) = \left| \frac{1}{(T^{*2} - T_0^2)^{1/2}} \right| \int_{T_0}^{T^*} \tau (T^{*2} - T^2)^{1/2} dT \quad (39)$$

which may be simply evaluated if the Thomson coefficient is proportional to the temperature. Unfortunately, this assumption is not generally justified, as indicated by MacDonald (35). For evaluation then, it is necessary to represent either the right or left side of the equation by a power series. The usual method is to represent the Thomson coefficient by a power series:

$$\tau = \alpha + \beta T + \gamma T^2 + \delta T^3 + \dots$$

It is then found that

$$\left(\frac{\Delta Q}{Q} \right) \left(\frac{E}{2} \right) = \alpha T^* + \beta T^{*2} + \gamma T^{*3} + \delta T^{*4} + \dots \quad (40)$$

where T^* is mathematically evaluated assuming the validity of the Wiedemann-Franz Law. The terms, α , β , γ , and δ are evaluated from the experimental data of $\frac{\Delta Q}{Q}$, and the Thomson coefficient is calculated in turn from these values.

A great deal of experimental work has been performed by many different investigators (36, 37) on indirect means of determining the Thomson coefficient. All of the techniques employ the Kelvin Relations to calculate the various thermoelectric parameters by measuring the

change of Seebeck potential (V) with respect to temperature (thermoelectric power) and then determining the Thomson coefficient with Equation (1).

It is impossible to describe all the significant contributions made to the knowledge of thermoelectrics through these measurements; however, one group which has contributed significantly, especially at low temperatures, was that headed by the late D.K.C. MacDonald (17).

In making measurements at very low temperature, MacDonald's group has made great use of the fact that certain elements and compounds are superconducting to relatively high temperatures. Since in the superconducting temperature range, these materials exhibit zero thermoelectric properties, any Seebeck voltage measured between this and another material will all be due to the second material. In this way absolute Seebeck potential can be measured directly.

The low temperature apparatus used by Christian, Jan, Pearson, and Templeton (38) for the determination of the absolute scale of lead, is similar to that used in low temperature thermal conductivity measurements (39). In their approach a couple was made between the lead and the superconducting Nb_3Sn , and the temperature gradient imposed by electrical means. The Seebeck voltage was measured quite accurately with a very sensitive potentiometer circuit. The temperature was then varied and a plot of thermoelectric power versus temperature was made. From the slope of this curve, the Thomson coefficient could be calculated from the Kelvin Relations.

The results obtained at low temperatures on various materials are

very interesting and rather surprising (40), in that the thermoelectric power varies a great deal, even to the extent of changing sign. The results do not agree with the classical theory of thermoelectrics (17), and as such have provoked a great deal of discussion (1,17,41) as to the nature of interactions taking place at low temperatures.

IV. EXPERIMENTAL

As previously indicated, the experimental apparatus necessary for the direct measurement of the Thomson heat must include means for applying a thermal and a D-C potential gradient, and adequate thermometry to measure both the thermal gradient and the thermal changes associated with the reversal of current flow. In order to avoid a long tedious analysis of heat losses, in which certain simplifying assumptions must be made, the system should also incorporate means of reducing radial heat losses from the sample to the surroundings. A calorimeter, to operate in the temperature range of $\pm 100^{\circ}\text{C}$, was designed and constructed to optimize each of these requirements.

Also incorporated in the experimental considerations was a sample design intended to improve on previous methods of detecting the thermal changes associated with the Thomson heat. The standard techniques generally employed, i.e. thermocouples welded to the sides of the specimen, or the standard optical techniques, do not give valid thermal measurements. The use of thermocouples in this manner, for example, changes the temperature distribution in the area of contact, while optical measurements at low temperatures are subject to errors introduced by diffraction and absorption. For this reason the samples in this investigation were designed with a very small axial hole extending the full length of the specimen, such that a well insulated thermocouple could be essentially embedded in the samples.

A. Calorimeter

The outer shell (F) of the calorimeter was constructed from a 3" cylinder of solid copper as shown in Figure 3. In order to prevent the current from flowing through the calorimeter shell, rather than through the specimen, the two end sections of the calorimeter were electrically insulated from each other by constructing the calorimeter in two sections, separated by a heavy rubber gasket (H), and held together by nylon bolts (M).

Massive copper cylinders, designed to slip fit into the end shells of the calorimeter, served as temperature control sinks (C). Each sink contained twelve evenly spaced, 1/4" holes, approximately 1/8" from the outside circumference, extending the length of the cylinder (N), into each of which were inserted hollow alumina insulating tubes. Heating coils of 0.030" chromel heating wire were in turn placed in the insulators. The twelve helical coils were connected in series and existed the calorimeter through insulated seals (D) in the top of the calorimeter to a 0 to 100 volt variac. A temperature control thermocouple well (E) was placed near the inside edge of each cylinder to insure maximum temperature control of the specimen. The chromel-alumel thermocouple in each of the sinks existed through insulated seals to the temperature controlling circuit. The copper top plates, to which the insulated vacuum seals were soldered, were bolted to the body of the calorimeter.

The temperature control sinks were designed to hold a 1" OD x 1" cylindrical sample heat sink, as shown in Figure 4. The

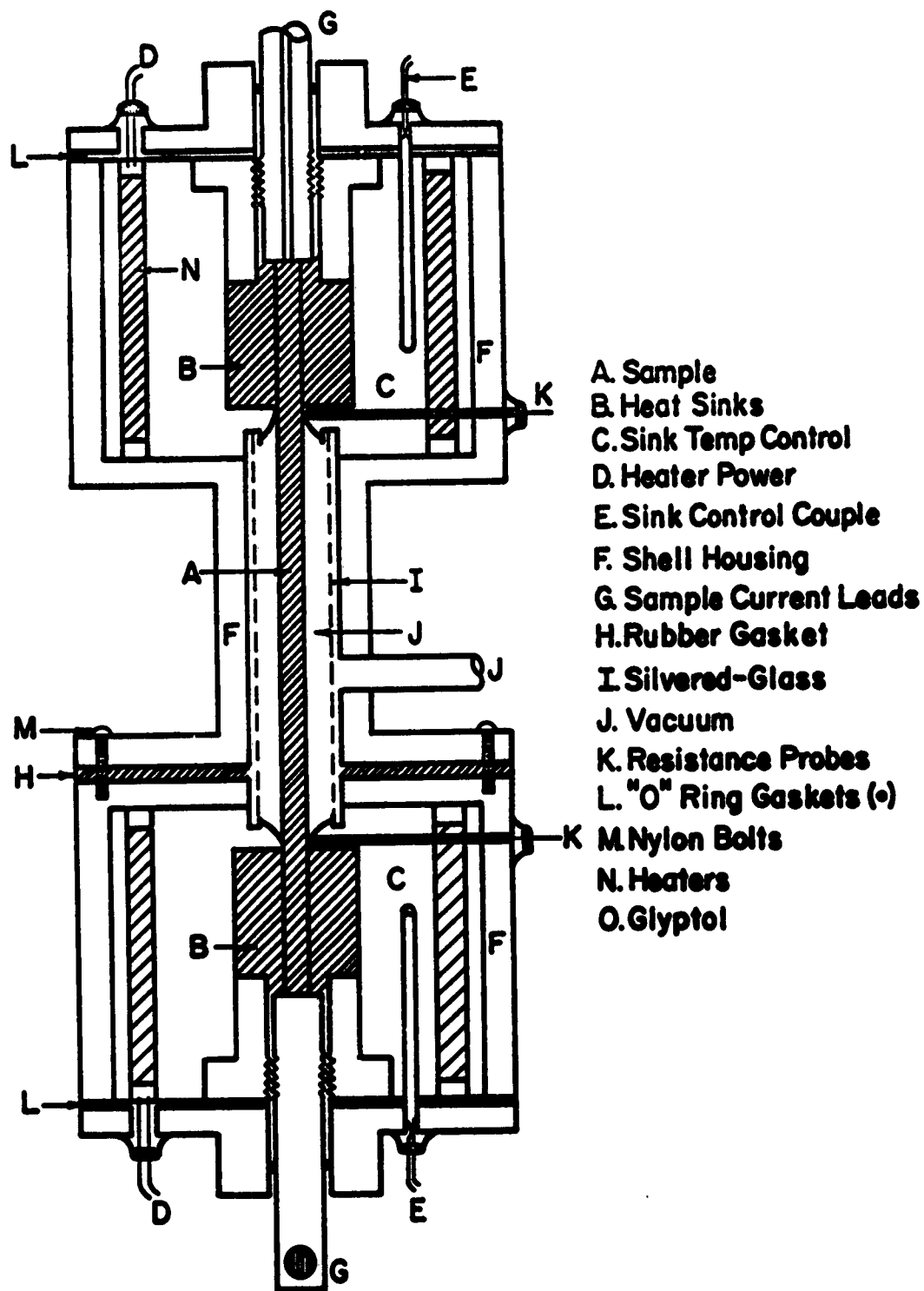


FIGURE 3 - Calorimeter for Thomson Coefficient determination

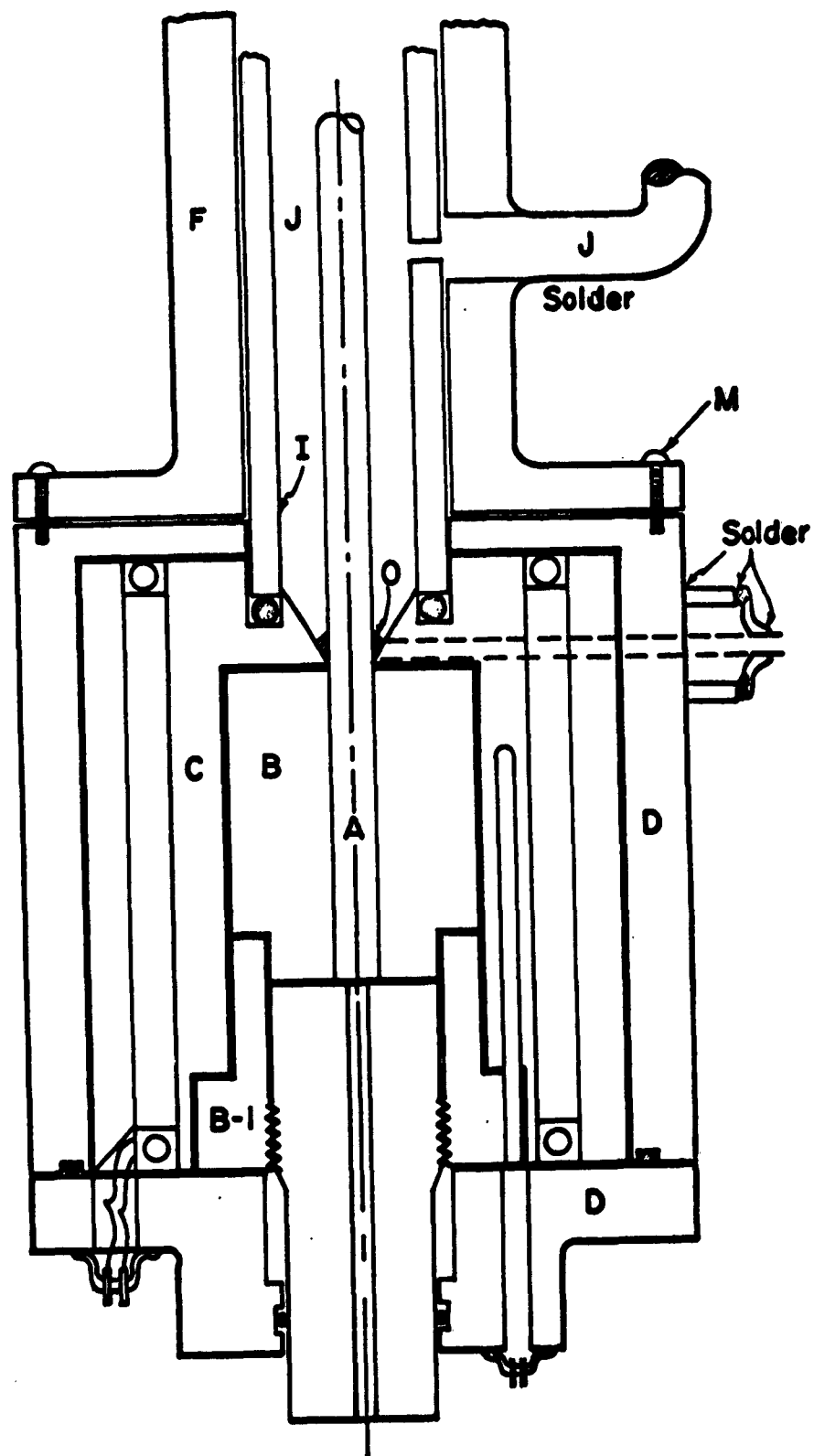


FIGURE 4 - Detailed diagram of end sink of calorimeter

sinks themselves were made of the material under test in order to minimize any Peltier effects between the sample rod and the heat sink. A hole, the size of the test sample, was bored in each of the sample heat sinks to allow maximum thermal contact with the specimen.

The test samples were 149.1 mm long, with an outside diameter of approximately 4.95 mm. A thermocouple hole, varying from 0.5 to 1.0 mm in diameter, depending upon the type of specimen being tested, was either milled or formed in the specimen during casting. An electrically insulated thermocouple was inserted in the hole to measure the temperature gradient and the change in temperature associated with the change in current.

During operation, the surface of the specimen was maintained under a vacuum to minimize radial heat losses from the sample to the surroundings. This necessitated a number of "O" ring seals as illustrated in Figure 3 and 4. It was also necessary to use a vacuum sealing varnish (Glyptol-General Electric) around the ends of the sample to prevent vacuum leaks along the interface between the sample and the sample heat sinks. To further minimize the heat losses from the sample by radiation, a silvered glass tube (I) was placed around the specimen.

B. Thermocouples

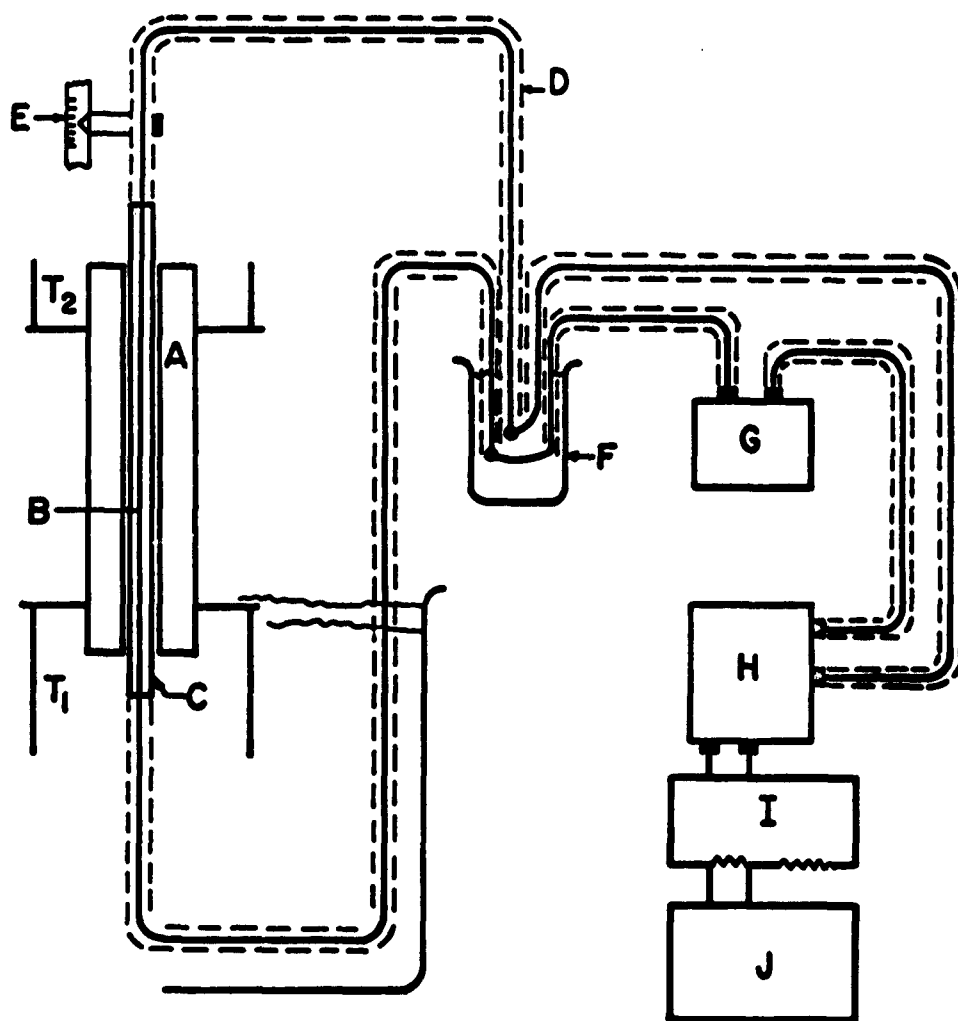
The preliminary investigations using chromel-alumel thermocouples for temperature measurements of the sample yielded output emfs which were quite erratic. Two sources of instability were

determined, i.e. inhomogeneities in the thermocouple wires and stray electromagnetic fields around the exposed thermocouple leads.

Inhomogeneities in the chromel and alumei thermocouple wires were found to give rise to stray Seebeck voltages when the wires were exposed to small temperature variations along its length. The inhomogeneities themselves act as point sources of voltages, which could be detected by the very sensitive measuring circuit. If, for example, the lead wires were subjected to stray air currents, this was sufficient to give rise to temperature variations along the wire, which could be detected by the sensing circuit. The addition of thermal insulation to the wire tended to reduce this effect, but not of sufficient magnitude to give satisfactory measurements.

Hultgren (42) indicated that selected, annealed copper-constantan thermocouples were of sufficient homogeneity to allow stable measurements of very small temperature differences. The actual wires to be used for the thermocouple were carefully selected by exposing small sections of the wire to sharp thermal gradients while the two ends of the wire were connected to a Nanovoltmeter (scale to 10^{-9} volts). Those lengths which gave the minimum output voltage under the thermal gradient were finally selected for the actual thermocouples.

In order to obtain the smallest diameter hole possible in the sample, the thermocouple bead was formed as a butt weld, such that the two leads could exit the sample in opposite directions, as shown in Figure 5. The bead itself was carefully filed to approximately



A. Sample
 B. Hot Junction
 C. Teflon Sleeve
 D. Shielding
 E. Cathotometer

F. Dewar
 G. Lindeck Micro-volt Source
 H. Nanovoltmeter
 I. Voltage Divider
 J. Brown Electron Recorder

FIGURE 5 - Temperature recording system

the same size as the wire and electrically insulated from the sample by forcing thin-walled teflon shielding over the thermocouple wire. Since high D-C currents flowed axially around the thermocouple, extreme care was exercised in assuring that no extraneous currents were transmitted to the thermocouple circuit. This was tested by placing the thermocouple in the sample and impressing high currents through the sample and examining the output for variations that could be attributed to the changes in the current. If any changes of this nature were detected, the thermocouple was removed and the insulation replaced.

Since variations in the thermocouple emf of the order of 0.05 microvolts were to be investigated, precautions which are not normally necessary in standard thermal measurements were required. To prevent interference from the ever present electromagnetic fields generated by control devices, all instrument leads, as well as the exposed section of the thermocouple, required very careful shielding to ground. In detecting the small differences in temperature associated with the Thomson heat, the cold junction also becomes more significant. Small voltage fluctuations associated with the melting ice were at first detected in the measurements. Substitution of a deep dewar flask, packed very tightly with crushed, distilled ice and a minimum of distilled water, provided a very stable cold junction. To further insure against any possible short circuits by electrochemical means between the two thermocouples, both cold junction terminals were electrically insulated.

C. Electrical Circuit and Controls

The output emf from the thermocouple was counterbalanced by the output emf of a Lindeck microvolt source (Model LE), such that all or any part of the thermocouple signal could be cancelled, as shown in Figure 5. In this manner, any emf variation over a desired temperature range acted as a source for a Keithley Nanovoltmeter (Model 148), such that differential changes in the order of $3 \times 10^{-5}^{\circ}\text{C}$ could be detected.

The one volt, full scale output from the Nanovoltmeter, regardless of the scale (1, 3, 10, 300 ... $\times 10^{-8}$ volts), was reduced by a fixed voltage divider network, the output of which acted as a source for a Brown Electronic Recorder (Model No. 15301876). The recorder was modified according to Kanda et al (43) to allow for a variable range from 0 to 50 mv and a variable zero point adjustment from 0 to 20 mv. In operation the zero point and the span of the Brown Recorder were calibrated with one scale of the Nanovoltmeter. Since the full scale output of the Nanovoltmeter was constant, regardless of the scale, macro or micro variations in temperature could be recorded directly on the recorder.

D. Power Supply to Sample

The electrical system used to supply the current for the specimen is shown in detail in Figure 5. The current was supplied by three fully charged 4 volt cadmium batteries (Cadmidyne) in parallel with an electro source D-C power supply (Model EPB). The current, regulated by a 4 ohm, 1000 watt Ohmite power rheostat

(Model U), flowed through the calibrated resistor of 90 mill mangan wire, through the current reversing switch and the sample. Contact resistance at each end of the terminals was maintained at a minimum. The 12 gauge copper wire used in the circuit was connected such that the circuit resistance was independent of the direction of current flow. The current in the circuit was constantly monitored during a particular investigation by using the voltage drop across the known manganan resistance as an emf source for a second modified Brown Electronic Recorder. The recorder was standardized with the output from the Lindeck microvolt source. Current changes in the sample of less than .01 amps could be detected with this circuit. The ammeter (Westinghouse - Model PX-4) was used to roughly select the current to be tested.

Various current reversing switches were tested in the circuit; however, it was found that a simple heavy duty double-pole-double-throw knife switch, modified such that the poles were physically within a few millimeters of each other at the open circuit position, gave practically zero switching time and a minimum of switching noise. In order to insure that the current did not change value in the switching process, identical short pieces of wire were carefully silver soldered into the circuit, so that the resistance of both paths were identical. It was found that the current changes were almost zero during the reversal of current.

F. Thermal Gradient

The temperature gradient in the sample was established by the

two end-temperature control heat sinks of the calorimeter as described in the calorimeter section. The temperature of the sinks were originally controlled by a multipoint Tabilaug Celest-Ray Controller (Model 48333), as activated by the respective control thermocouples placed in the end heater sinks. Various temperature gradients for the sample could be chosen by presetting the desired temperature on the Celest-Ray unit. In the first series of experiments it was noted that the sample thermocouple was detecting slight changes in temperature, corresponding to the on-off cycle of the heaters. For this reason the Thomson heat data to follow was obtained with the heater sinks under static heating conditions; that is, the high temperature end-heaters were subjected to a constant voltage input to the heaters at the high temperature end and the sink allowed to achieve thermal equilibrium. The heat flowing down the rod was continually removed from the low temperature end of the calorimeter by immersing that end in a five gallon constant temperature bath.

F. Samples

The selection of the test materials for this study was made on the basis of their thermoelectric properties. Lead was chosen for the investigation since it is generally accepted as a standard thermoelectric reference material, based on its very low Thomson coefficient, i.e. almost no variation of thermoelectric power with temperature (cf. Equation 1). Thus, any thermoelectric data obtained between lead and another material is often considered

to be an absolute value of the thermoelectric properties of the second material. Nickel, on the other hand, was selected on the basis of its very high Thomson coefficient in the temperature range to be studied. The choice of these two metals should, therefore, demonstrate the extreme interactions taking place in any measurement of the Thomson coefficient; the difference in their Thomson coefficient values is approximately two orders of magnitude - Pb \approx 0.30 μ v/deg. and Ni \approx 35 μ v/deg.

The lead used in this investigation was obtained from the American Smelting and Research Corporation of New Jersey. The major constituents in the lead bars were as follows:

Lead	99.999 + %
Magnesium	< 0.5 PPM
Silicon	< 0.5 PPM
Iron	< 1.0 PPM
Copper	< 1.0 PPM
Oxygen	< 5.0 PPM

Several different approaches were used in an attempt to obtain a 0.020" coaxial hole through the length of the sample. The most satisfactory results were obtained by first melting the lead in a pyrex tube under an argon atmosphere and then casting the liquid metal into a 5 mm ID pyrex tube, which was held at 325°C by a nichrome heating coil wrapped around the glass. Two 5 mm iron slugs, with 25 mill center holes, were sealed at opposite ends of the glass to hold the 20 mill iron wire in the center of the

tube. A three pound weight was suspended from the lower end of the wire to hold the wire straight. To prevent leakage of the liquid lead out of the wire exit hole, wet asbestos paper was wrapped around the base of the tube. Once the lead had been cast the variac was gradually reduced to zero. The glass was then thermally cracked and finally removed from the specimen by careful grinding. Since iron and lead are completely immiscible, the iron wire could usually be removed by simply pulling the wire through the specimen.

The lead sample was then mounted in the calorimeter by placing one end of the sample in one of the lead heat sinks and then coating the sample where it met the sink with the vacuum varnish. The sample and the sink were then carefully guided into the calorimeter. Once the sample was in place in the opposite end of the calorimeter, the sample-heat sink junction was given a light coat of varnish and the second lead sink slipped into place over the sample into the copper heating sink. At this time the thermocouple was inserted and the leads passed through the electrical connectors as described earlier.

The nickel was obtained from the United Minerals and Chemical Corporation of New York City. The major constituents in the nickel rods were as follows:

Iron	< 4 PPM
Silicon	< 3 PPM
Calcium	< 1 PPM
Copper	< 1 PPM
Magnesium	< 1 PPM
Silver	< 1 PPM

Since it was almost impossible to cast or drill a 0.5 to 1.0 mm hole over a length of 150 mm in the nickel specimen, the sample had to be prepared from two 5 mm diameter rods. Two and one-tenth centimeters were milled longitudinally from one of the nickel rods and then an .8 mm slot was milled the entire length of the sample. Two and nine-tenths centimeters were then milled from the second sample, the remaining section being placed on top of the first milled section and the two section then Heli-Arc welded the length of the rod.

The same technique was used to mount the nickel specimen in the calorimeter as used with the lead specimen.

G. Experimental Techniques

There were basically three operational techniques employed in obtaining the value of the Thomson coefficient. Of these methods, two were essentially new techniques developed in this investigation from the fundamental equations governing the longitudinal flow of heat in a rod, i.e.

$$\frac{dH}{dt} = J^2 \rho + J_T \frac{dT}{dx} + k \frac{d^2 T}{dx^2} \quad (30)$$

The third technique was that suggested by Nystrom, in which the Thomson coefficient was calculated from the change in current necessary to compensate for the change in heat obtained with reversal of current flow, i.e.

$$J^2 \rho + J\tau \frac{dT}{dx} = (J + \Delta J)^2 \rho - (J + \Delta J)\tau \frac{dT}{dx} \quad (33)$$

Method I, the first technique to be examined was based on non-equilibrium considerations of Equation (30). When current is first applied to a simple heater coil, almost all of the heat is first absorbed by the sample, and little, if any, is lost to the surroundings. Mathematically, this is based on the equation for the driving force for heat losses:

$$hA(T_{Sa} - T_{Su}) \quad (41)$$

where

h = heat transfer coefficient

T_{Su} = temperature of the surroundings

T_{Sa} = temperature of the coil

In the first few seconds there is very little difference between T_{Su} and T_{Sa} , and, therefore, this term may be assumed to be zero.

Applying this reasoning to the basic equation governing heat flow in a sample such as used in Thomson heat investigations, the last term in Equation (30) becomes zero, and the equation can be rewritten:

$$\frac{dH}{dt} = J^2 \rho + J\tau \frac{dT}{dx}$$

The initial runs were made on the pure lead samples, in which the current was applied in one direction only until a definite slope, $(dT/dt)_1$, was established. As soon as this slope could be measured, the current was then reversed and a second slope established, $(dT/dt)_2$, due to the different rate of heat input. Mathematically, the Thomson coefficient could be calculated from the following considerations:

For current in one direction:

$$mc\left(\frac{dT}{dt}\right)_1 = J^2\rho + J\tau \frac{dT}{dx} \quad (42)$$

for current flow in the opposite direction:

$$mc\left(\frac{dT}{dt}\right)_2 = J^2\rho - J\tau \frac{dT}{dx} \quad (43)$$

subtracting Equation (43) from Equation (42)

$$mc\Delta \frac{dT}{dt} = 2J\tau \frac{dT}{dx} \quad (44)$$

Another analysis, based on the same non-equilibrium equations, is to simply measure the initial slope, (dT/dt) , for either direction of current flow and calculate the Thomson coefficient from this measurement, i.e.

$$mc\left(\frac{dT}{dt}\right) = J^2\rho + J\tau \frac{dT}{dx} \quad (45)$$

$$\tau = \frac{1}{J \frac{dT}{dx}} (mc \frac{dT}{dt} - J^2\rho) \quad (46)$$

or, for the opposite direction of flow:

$$\tau = \frac{1}{J \frac{dT}{dx}} (J^2\rho - mc \frac{dT}{dt}) \quad (47)$$

The other new technique used to calculate τ , Method II, is based on equilibrium considerations of the basic equation. At equilibrium the sample is not changing temperature with time and Equation (30) becomes:

$$-k \frac{d^2 T}{dx^2} = J^2 \rho + J\tau \frac{dT}{dx}$$

This equation has been solved in Appendix B, for a general position (x) in the sample and then specifically for $x/2$. To obtain τ for a general position in the sample it is necessary to use a computer. The known parameters, such as resistivity, thermal conductivity, end temperatures, and current, were substituted into the equation for various values of τ . The computer is programmed such that a plot of both directions of current flow was made of position versus temperature, its derivative with respect to position, and the difference in temperature between the two different directions of current flow. The print out from the computer for 1 of 50 values of τ was as follows:

$$\tau = 30 \times 10^{-6} \quad J = 25$$

x/L	θ	θ_R	θ'	θ'_R	$\Delta\theta$
.1	.1009	1.008	.1002	1.001	.0008
.2	.2017	1.006	.2003	1.001	.0014
-	-	-	-	-	-
-	-	-	-	-	-
1.0	1.0000	.9896	.9999	.9980	.0000

where

$$\theta = \frac{T(x) - T_o}{T_L - T_o} \text{ for current in one direction}$$

$$\theta_R = \frac{T(x) - T_o}{T_L - T_o} \text{ for current in opposite direction}$$

$$\theta' = d\theta/dx$$

By substituting actual data in the equation and comparing the actual experimental values with the set of values obtained from the computer, a value for τ could be obtained.

A much simpler method of determining τ is to measure the change in temperature at the center of the sample and simply use the equation developed in the latter part of Appendix B. This is by far the easiest and most direct method of measuring the Thomson coefficient. It has been developed from first principles and completely does away with any need of changing the current, which was found to be rather insensitive in this investigation.

V. RESULTS AND DISCUSSION

Method I, the non-equilibrium, change in slope technique, was used first to measure the Thomson coefficient of lead. A multitude of runs were made with these samples; however, stray fields were of such magnitude, relative to the small changes associated with the Thomson heat of lead, that the results were, in general, quite erratic. The only reproducible results were obtained late at night when the fields around the measuring equipment were at a minimum. Two of the more stable runs on the lead samples are shown in Tables 1A and 1B.

TABLE 1A

Values of the Thomson coefficient of Lead Using Method I

Base Temperature = 41.0°C $dT/dx = 2.2^{\circ}\text{C/cm}$		
Amps	$d\mu v/dt$	Thomson coefficient μv volts/degree
3.0	0.0008	- .412
3.96	0.0009	- .339
5.10	0.0013	- .380
5.98	0.0016	- .398
6.85	0.0013	- .283
		Average $\tau = 0.360 \pm 0.041$ $\times 10^{-6}$ volts/deg.

TABLE 1B

Values of the Thomson coefficient of Lead Using Method I

Amps	$d\mu v/dt$	Thomson coefficient μ volts/degree
3.92	0.0005	- 0.189
5.16	0.0017	- 0.498
5.98	0.0009	- .235
6.87	0.0013	- .283
		Average $0.304 \pm 0.099 \times 10^{-6}$ volts/degree

One of the calculations is as follows:

$$mc \, dT/dt = 2J\tau \, dT/dx$$

for lead

$$m = 11 \text{ gm/cc (44)}$$

$$c = .03 \text{ cal/gm-}^\circ\text{C (44)}$$

$$(11 \text{ gm/cc})(.03 \frac{\text{Cal.}}{\text{gm-}^\circ\text{C}})(\frac{1 \text{ watt}}{.239 \text{ cal/sec}})(\frac{1^\circ\text{C}}{42.1\mu\text{v}})(\frac{d\mu v}{dt}) = 2 (\frac{3.0 \text{ amps}}{2})(2.1 \frac{^\circ\text{C}}{\text{cm}})$$

$$\tau = .412 \times 10^{-6} \mu\text{v/deg}$$

The average results obtained with this technique is fairly close to the value of .30 $\mu\text{v/deg}$, given by Christian et al (45); however, the scatter is fairly high. To test the validity of this experimental approach, two alterations were made in the approach. The first change was made in order to make the measurements further from thermal equilibrium, where the heat losses were more likely to be zero. This was accomplished by changing to much faster recording rates in the Brown

Electronic Recorder and using a single slope to calculate the Thomson coefficient, i.e.

$$mc \frac{dT}{dt} = I^2 \rho + I \tau \frac{dT}{dx}$$

The second change was to simply use nickel samples, where the Thomson coefficient is so high that the stray fields would only be a small percentage of the Thomson heat.

The experimental results obtained using this technique were found to have much less scatter when the electron flow was in the direction of decreasing temperature. The slopes of the curves for this direction of flow were quite linear in the first few seconds and gradually changed slope as the heat losses became more pronounced. With electron flow in the opposite direction, i.e. in the direction of increasing temperature, it was difficult to obtain reproducible results. During the first few seconds of such a run, a definite slope would first be established, but would suddenly give way to a much steeper slope as shown in Figure 6. This behavior is believed to be due to some fundamental process taking place in the sample, which is not encountered in the more common equilibrium considerations. In making calculations of the Thomson coefficient with opposing thermal and electron flow, the earliest slope was used to make the calculations. This is admittedly questionable, but the results do agree better with those obtained with the opposite flow, although they are not nearly as reproducible.

The average of four runs, ignoring small differences in experimental conditions, is shown in Table 2.

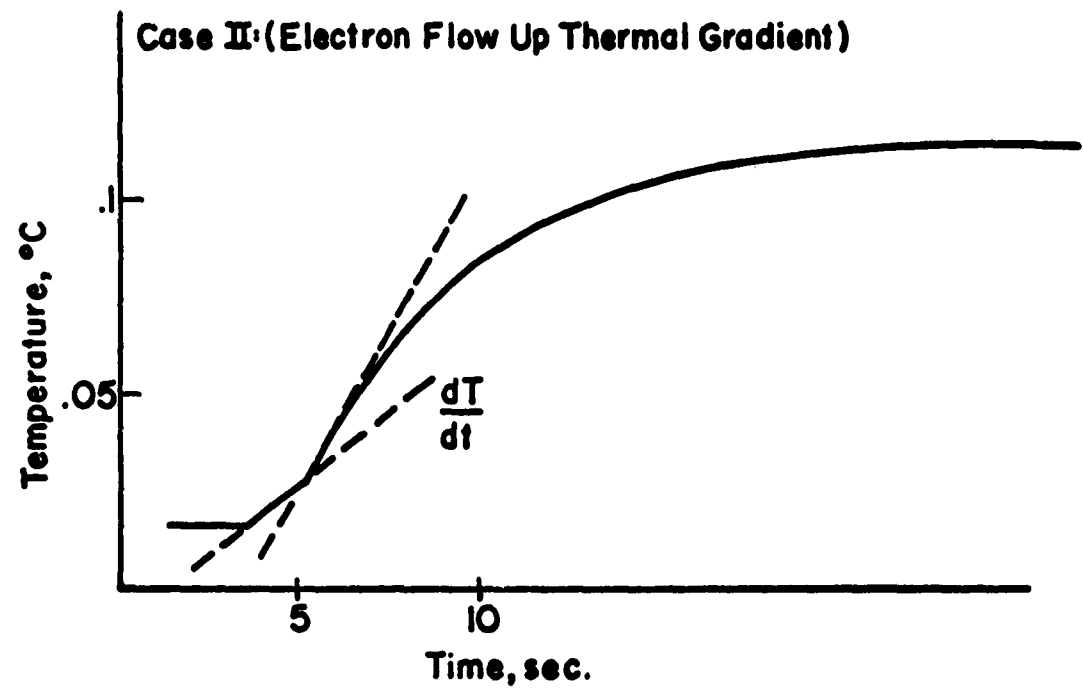
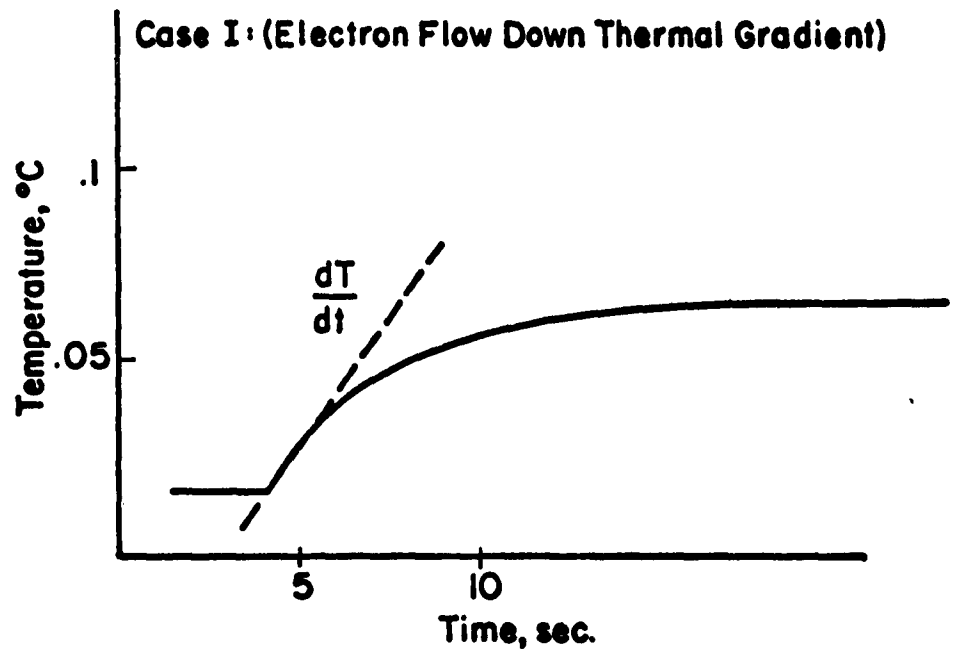


FIGURE 6 - Sketch of curves obtained with two directions of current flow in a nickel sample

TABLE 2

Values of the Thomson coefficient of Nickel, Using Method I

$T_{\text{Base}} = 41.2^{\circ}\text{C} \quad dT/dx = 2.5^{\circ}\text{C}$				
Amps	A^*		B^*	
	$dT/dt, ^{\circ}\text{C}/\text{sec}$	$-\tau, \mu\text{v}/\text{deg}$	$dT/dt, ^{\circ}\text{C}/\text{sec}$	$-\tau, \mu\text{v}/\text{deg}$
2.98	.0094	24.74	.0318	42.8
3.96	.0197	30.93	.0381	13.81
5.08	.0279	39.74	.0676	36.60
5.96	.0464	30.79	.0822	20.05
6.78	.0710	35.52	.1340	45.20
	Average $= -32.34 \pm 4.23 \mu\text{v}/\text{deg}$		Average $= -31.69 \pm 10.81 \mu\text{v}/\text{deg}$	

Where A^* = values for electron flow in the direction of decreasing temperature

B^* = values for electron flow in the direction of increasing temperature

A sample calculation is as follows:

$$I = 3.96 \text{ amps}$$

$$mc \frac{dT}{dt} = J^2 \rho - J\tau \frac{dT}{dx}$$

where for nickel

$$m = 8.75 \text{ gm/cc (46)}$$

$$c = .11 \text{ cal/gm-}^{\circ}\text{C (46)}$$

$$(8.75)(.11) \frac{dT}{dt} = \left(\frac{3.96}{.2}\right)^2 (7.7) \times 10^{-6} - \frac{3.96}{.2} (2.5)\tau$$

$$\tau = 30.93 \mu\text{v}/\text{deg}$$

Several runs were made using the standard technique of changing the current to compensate for the difference in the heat produced on switching the direction of current to calculate the Thomson coefficient, i.e. Method III. This technique was used to see how well the experimental apparatus was performing with respect to the arrangement used by other investigators. The exact technique employed for this measurement can best be understood with reference to Figure 7. The current was first applied to the sample such that the Thomson heat was adding to the Joule heat and the thermocouple voltage noted when equilibrium was obtained, point 1 in Figure 7. The current was then reversed and the equilibrium voltage measured with this direction of current flow, point 2. The current, with the direction of current now opposite to that first applied, was then arbitrarily increased and the associated change of the thermocouple was measured once an equilibrium temperature was achieved, point 3. The current was further adjusted, points 4 and 5, until the equilibrium plateau was very close to that first achieved, point 1. This data could be used in a direct calculation of the Thomson coefficient, from Equation (33); however, a better average result can be obtained for a given set of boundary conditions by continuing the same procedure to higher currents. Starting at point 5, the current can be increased to some new value, point 6, noting associated changes in emf output, and then reversing the current flow, point 7. The current could then be decreased arbitrarily, point 8, and then more exactly, points 9 and 10, until the emf corresponding to point 6 is obtained. With the experimental arrangement used in this investigation the current was

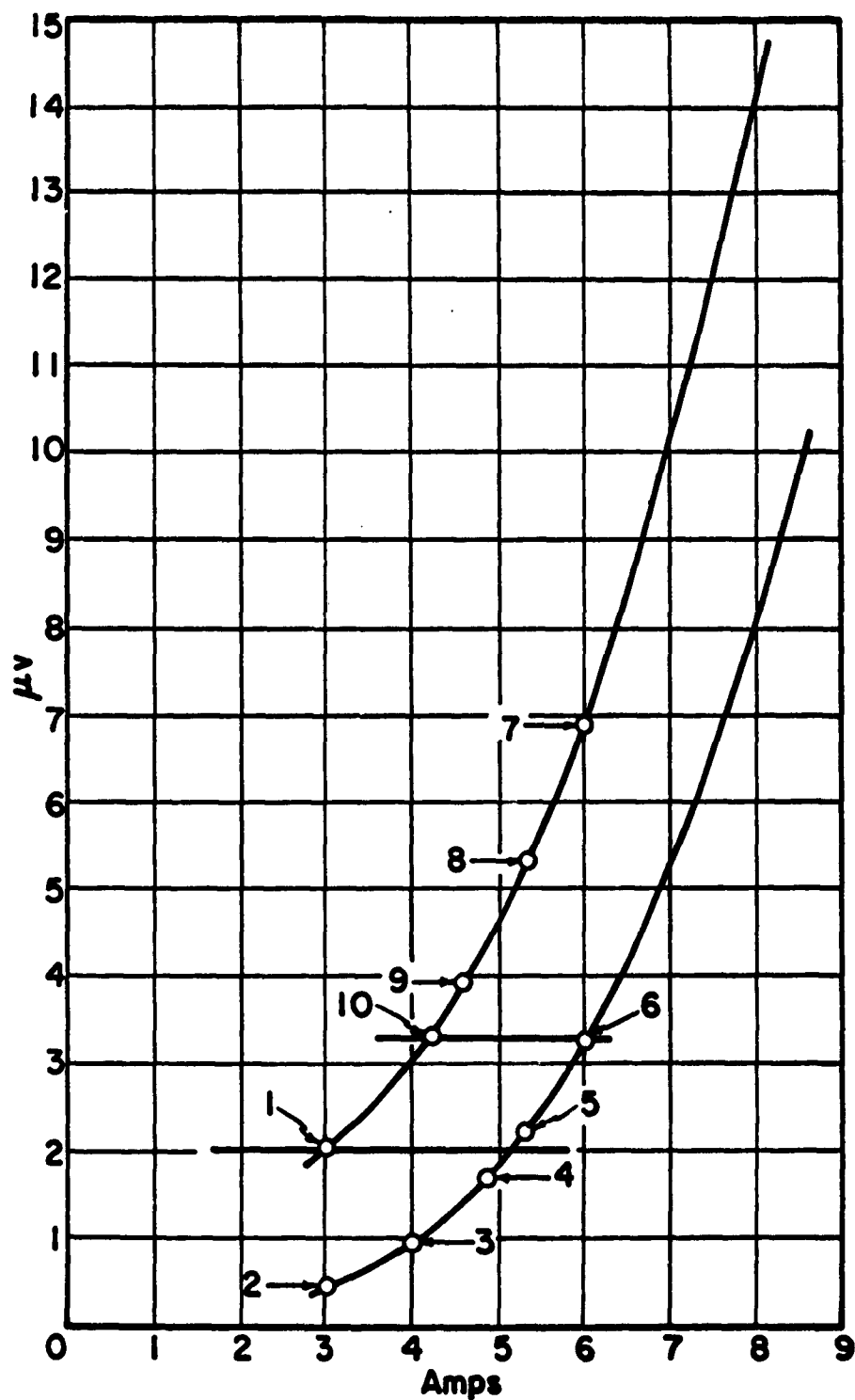


FIGURE 7 - Sketch of method for determining Thomson Coefficient

varied up to approximately 8 amps and then back down to 3 amps.

In order to cover this current range and maintain the precision necessary for these calculations, it was necessary to cancel part of the signal from the thermocouple in going from one measurement of the Thomson coefficient to another, i.e. from points 5 and 6. The readjustment might possibly have introduced a slight shift in the data between points such as 5 and 6. It should be emphasized that this in no way affects the calculated values of the Thomson coefficient, since no adjustments were necessary in the series of points 1 through 5 and 6 through 10. Although there might be some small errors by presenting the data as a graph, it was felt that this type of presentation provided much better means of comparison with data calculated by other means. Figures 8, 9, and 10, are the graphs plotted from the data obtained in this way. The resulting values of the Thomson coefficient, calculated from the equation:

$$\tau = \frac{\rho \Delta J}{dT/dx}$$

are shown on the respective graphs. The dashed lines in Figure 10 is a plot of the results obtained from the computer technique using values of τ indicated on the graph, where the boundary conditions are the same as those using the experimental run. The results obtained from the two different techniques appear to agree reasonably well.

Calculations using the simplest of all techniques, developed in the latter part of Appendix B, are shown in Table 3. This technique could be applied to all the data obtained in Method III, since it is

$T_{Base} = 40.0^{\circ}C$; $T_1 = 28.9^{\circ}C$; $T_2 = 51.2^{\circ}C$

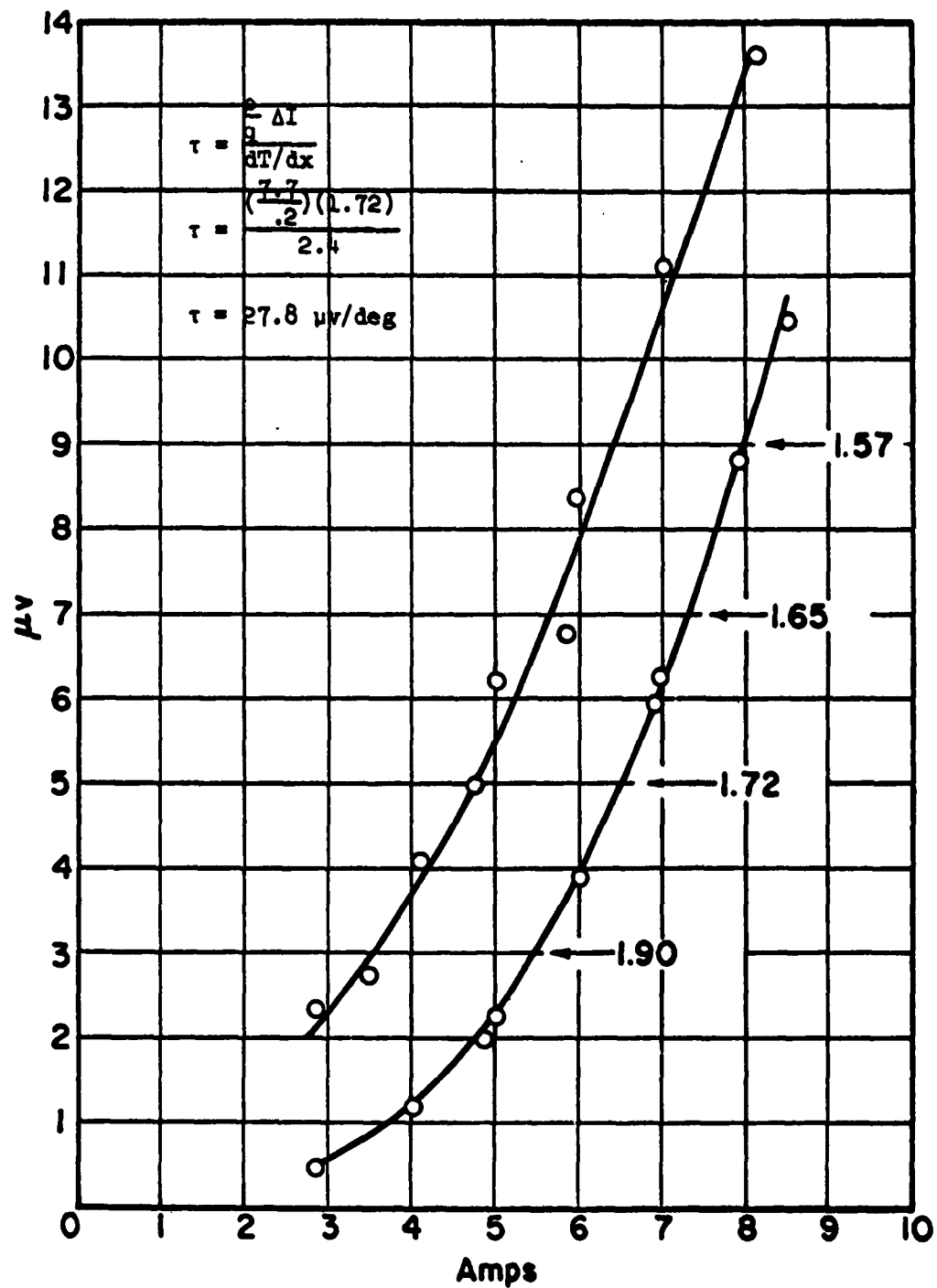


FIGURE 8 - Data obtained on nickel samples using Method III - specific boundary conditions (numbers in body of graph are values of ΔI)

$T_{Base} = 42.15^{\circ}C$; $T_2 = 55.1^{\circ}C$; $T_1 = 30.0^{\circ}C$

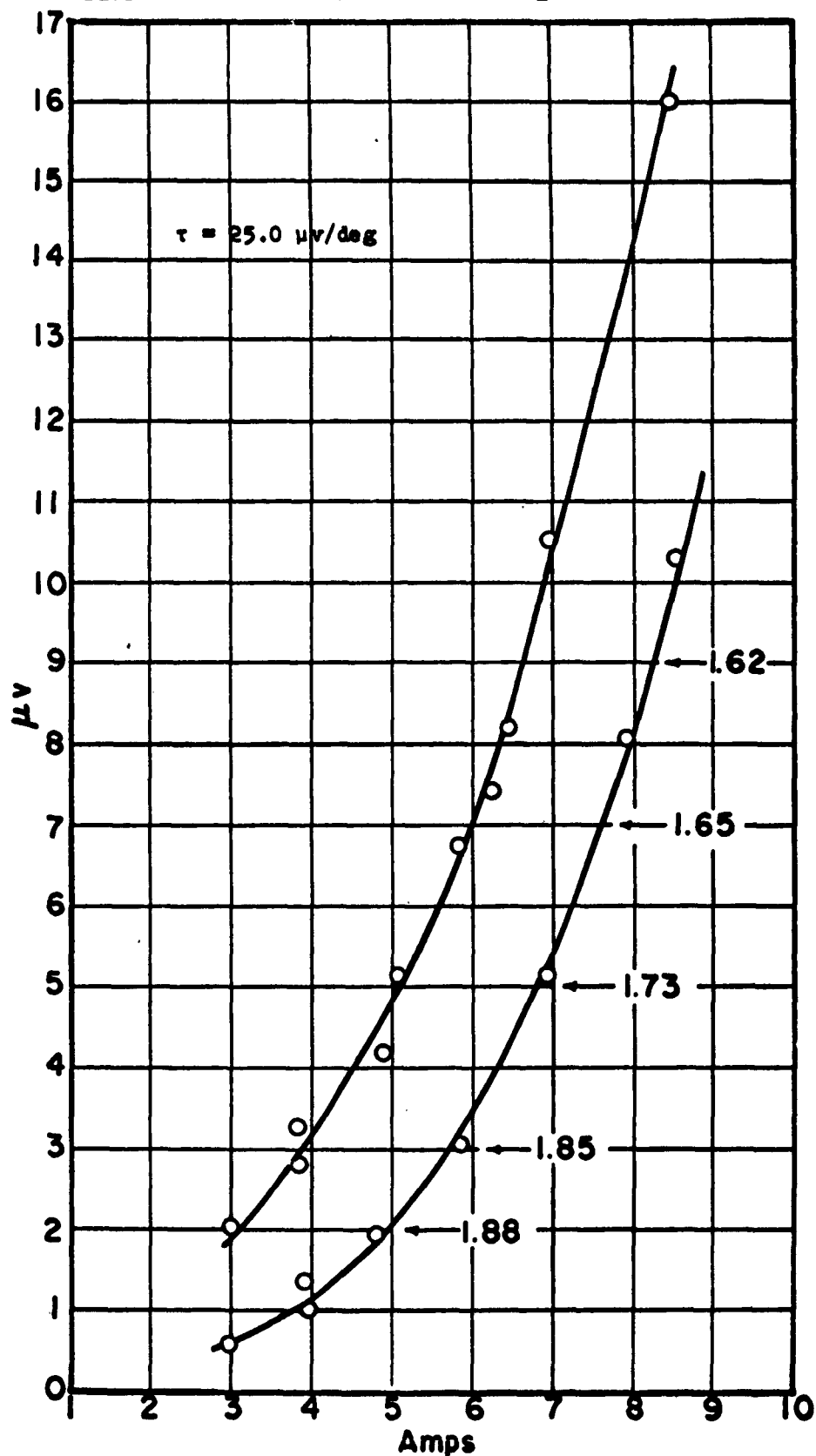


FIGURE 9 - Data obtained on nickel samples using Method III - specific boundary conditions (numbers in body of graph are values of ΔI)

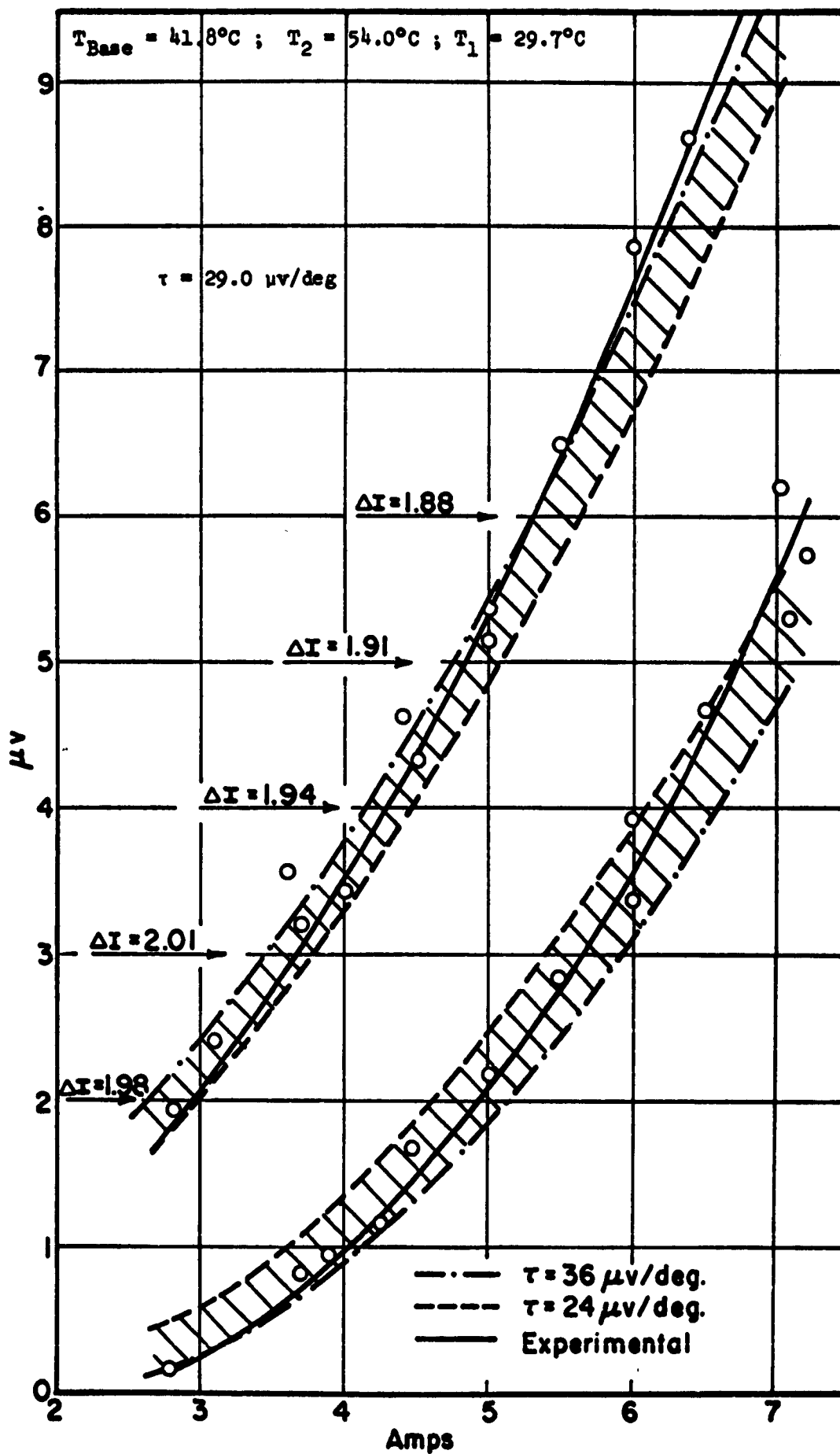


FIGURE 10 - Comparison of Method II and Method III for calculating the Thomson Coefficient

also an equilibrium technique using data obtained at $x/2$. The only difference being, that this latter technique is much easier, in that the current need not be changed. The only data necessary is the change in equilibrium temperature, which is the first data obtained in Method III. The Thomson coefficient can simply be calculated from the equation:

$$\tau = \frac{4k\Delta T}{(T_L - T_0)JL} \quad (48)$$

TABLE 3

Values of the Thomson coefficient Using Method II, Special Case

$T_1 = 27.8^\circ\text{C} \quad T_2 = 52.6^\circ\text{C} \quad T_{\text{Case}} = 40.1^\circ\text{C}$ $k = .594 \text{ watts/cm (44)}$ $L = 9.3 \text{ cm}$		
Amps	ΔT	$-\tau, \mu\text{v/degree}$
2.96	.048	33.3
4.02	.048	24.6
4.88	.067	28.2
5.98	.107	36.8
6.92	.098	29.0
		Average $= -32.4$ $\pm 4.0 \times \mu\text{v/deg}$

For the sake of comparison, this equation has been used to calculate the values of τ from the data used in Figure 10. The values of the Thomson coefficient obtained in this way are given in Table 4. Any difference between the 2 techniques is probably due to small radial heat losses which were not taken into account in the equation developed

in Appendix B and the fact that different coefficients were used in the two techniques to calculate the Thomson coefficient.

TABLE 4
Thomson coefficient Calculations from Previous Data, Using Method II -
Special Case

Amps	$\Delta\mu v$	$-\tau, \mu v/\text{deg}$
3.	1.81	29.9
3.5	2.17	31.0
4.0	2.50	31.2
4.5	2.85	31.6
5.0	3.22	32.2
5.5	3.57	32.5
6.0	3.95	32.9
6.5	4.25	32.7
		Average = -31.8 $\mu v/\text{deg}$

Values of the Thomson coefficient of nickel and lead in the temperature range studied in this investigation are quite limited. In order to make a direct comparison of these data with the results obtained from other studies, it was necessary to make extrapolations of both Thomson coefficient data and thermoelectric power data, which was then differentiated to obtain values for the Thomson coefficient.

Using the results obtained by Borelius (47), the Thomson coefficient of lead in the temperature range of 40.0°C, would be - 0.57 $\mu v/\text{deg}$, which is in rough agreement with the average value of - 0.33 $\pm .09 \mu v/\text{deg}$ found in this study. Borelius indicated that his values

could have been in error, as his equipment had not been properly standardized. Extrapolating the thermoelectric power results obtained by Pearson et al (40), to the temperature range around 40.0°C, and then taking the derivative of this curve, values of approximately - 0.30 $\mu\text{v}/\text{deg}$ are obtained for lead, which agrees quite closely with the values obtained for lead using the change in slope technique. The values calculated with the change in slope technique, however, are quite scattered. Since Pearson has not reported any limits in his work, it is difficult to make a comparison between the two means of measurement.

Nickel has been studied by Borelius (47), Rudnitskii (13), and Grew (48). Borelius' results indicate a value of - 18.0 $\mu\text{v}/\text{deg}$ at 41.0°C, although he freely admits that this value is probably not too valid, since his samples were relatively impure and the calculations were made with a questionable standard. Rudnitskii's results indicate a value of approximately - 32.0 $\mu\text{v}/\text{deg}$ for nickel at 41.0°C, which agrees much better with the value of approximately - 30.0 \pm 5.0 $\mu\text{v}/\text{deg}$ obtained in this investigation. He has not, however, given any indication of the amount of scatter which may have been present. Extrapolating Grew's measurements of thermoelectric power to 41.0°C and taking the derivative of this curve, yields a value of approximately - 28.0 $\mu\text{v}/\text{deg}$ for nickel, which again agrees very well with the data obtained in this study. Once again, no indication is given in regard to the possible amount of error.

As indicated above, the values of the Thomson coefficient of both lead and nickel obtained in this investigation, were apparently the first to be calculated from direct measurements in the temperature range of 40.0°C.

There seems to be no apparent explanation for the change in slope encountered with opposing thermal and electrical flows, in the non-equilibrium technique. If this phenomena were due to some type of phonon-electron interaction, one would expect the effects to be completed in a matter of micro-seconds. As this anomaly was generally encountered a second or two after the initiation of current flow, such an explanation seems quite inadequate. Magnetic effects associated with the initiation of the D-C current were also ruled out, since these fields would be stationary in a very short time. To insure that effects such as these were not delayed between their generation and recording, a rapidly changing voltage from the Lindeck microvolts source was impressed on the measuring network, which indicated that the circuit had a very fast response time. This phenomenon does seem to be attributable to some interaction taking place in the sample, which only occurs with opposing thermal and electrical flows.

VI. SUMMARY AND RECOMMENDATIONS

In general, this investigation presented the fundamental concepts of the Thomson heat and applied these concepts to measure values of the Thomson coefficient. More specifically, the investigation can be separated to include the following:

1. Development of the non-equilibrium techniques for the direct measurement of the Thomson coefficient.
 - a) This included the change in slope technique, and
 - b) Single slope technique.
2. Development of a new approach to the equilibrium techniques for determination of the Thomson coefficient.
 - a) This included a method for a general position in the sample, and
 - b) The special case of measurements made at $x/2$.
3. The design and utilization of an experimental apparatus to examine the various approaches for a direct determination of the Thomson coefficient. The samples in this investigation were designed to avoid erroneous temperature measurements. In either welding the thermocouple to the side of the specimen or drilling surface holes in the specimen, the actual temperature distribution and electrical flow is disturbed in the area at which the measurement is being made. Although the effect may be rather small, it could amount to an appreciable error in relation to the small changes associated

with the Thomson heat. With the placement of the thermocouple down the center of the sample, as in this investigation, these effects would be minimized; this, however, may introduce small losses of heat down the center of the sample, which undoubtedly have some small affect on the experimental values. Theoretically, the best method for avoiding these difficulties is the approach used by Nystrom, i.e. an optical thermal measurement. In practical application this approach has proved to be no more reliable than the others, since it is usually limited by emissivity of the radiant energy from the sample and absorption in the optical path.

4. Application of these new techniques, as well as standard techniques, to calculate the Thomson coefficient of lead and nickel.
 - a) Method I - Non-equilibrium Technique - This technique proved to be fairly reliable, with a minimum of scatter, for electron flow in the direction of decreasing temperature. The results, however, were not reproducible for the current flow in the opposite direction.
 - b) Method II - New Equilibrium Techniques - The special case of this technique, i.e. measurements made at a point half way between the two end sinks, is by far the simplest approach for calculating the Thomson coefficient. This technique does require very small radial heat losses.
 - c) Method III - Standard Technique - The adjustment of the current to exactly compensate for the loss or gain of

Thomson heat was found to be quite difficult to control with the experimental arrangement used in this investigation. The results, however, were fairly reproducible and reliable, as long as the assumption is made that there is no change in the heat loss mechanism with change in current flow.

The measurement of the small changes occurring in this investigation were hampered by stray electromagnetic fields in the laboratory. This was validated by purposely introducing electromagnetic source or magnetic fields during an experimental run. The stray fields were circumvented in part by shielding the lead wires as much as possible, by minimizing loops, and making runs late at night when the fields were at a minimum. It is felt, however, that the accuracy and reproducibility of the data was limited by these fields. For this reason it is recommended that future studies of this nature be conducted in a well grounded cage.

The anomaly encountered with opposing electrical and thermal currents presents an interesting problem, the solution of which was beyond the scope of this investigation. An investigation of the mechanisms giving rise to such an effect could possibly lead to a better understanding of electron-phonon interaction and should be pursued on this basis.

APPENDIX A

A simple heater coil will be considered to show how various equilibrium temperatures can be achieved by simply changing the rate of heat input. The general equation governing the flow of heat into the coil is as follows:

$$\dot{Q}_I = \dot{Q}_A + \dot{Q}_L \quad (1A)$$

or more explicitly

$$I^2 \rho V = cm \frac{dT}{dt} + hA(T_{Sa} - T_{Su}) \quad (2A)$$

where:

$$I^2 \rho V = \text{rate of electrical heat input}$$

$$cm \frac{dT}{dt} = \text{rate of heat accumulated in the coil:}$$

c = specific heat and m = density

$$hA(T_{Sa} - T_{Su}) = \text{rate of heat losses to the surrounding:}$$

h = heat transfer coefficient

A = area

T_{Sa} = sample temperature

T_{Su} = temperature of surroundings

This equation has a solution of the form:

$$T_{Sa} = \frac{I^2 \rho V}{hA} - \frac{I^2 \rho V e^{-t\theta}}{hA} + T_{Su}$$

A plot of the various heats versus time is shown in Figure 11.

According to Equation (1B), if the rate of heat input is now increased the previous curves will be shifted up as shown in Figure 12,

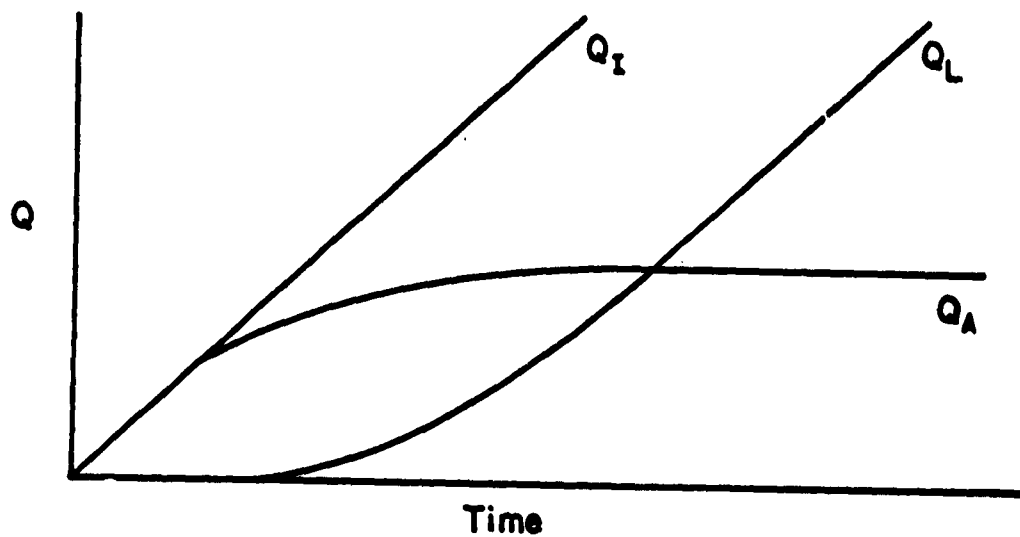


FIGURE 11 - Approach to equilibrium of a simple heater coil

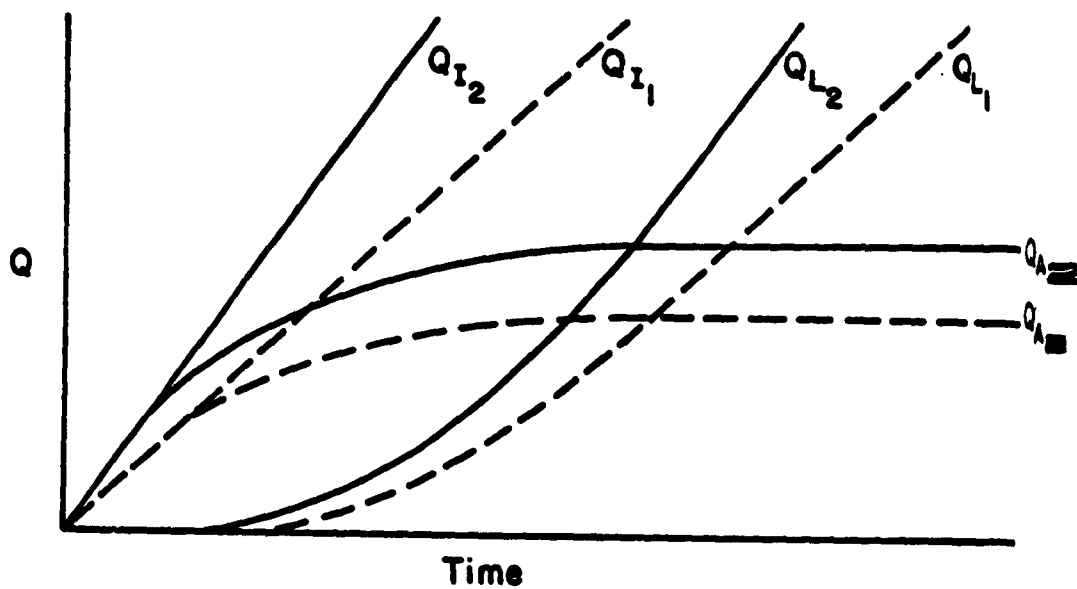


FIGURE 12 - Approach to equilibrium of a simple heater coil for different rates of input

coming to a different equilibrium temperature, assuming the heat transfer coefficient does not change with change of current flow.

Inclusion of the Thomson heat in the \dot{Q}_I term in the previous analysis will not have an appreciable affect on the shape of the curves.

APPENDIX B

The simplified equilibrium equation governing heat flow out of a rod, where radial heat losses are considered to be negligible, is:

$$-k d^2 T / dx_1^2 = J^2 / \sigma + \tau J \frac{dT}{dx_1} \quad (1B)$$

The solution to this equation, in dimensionless analysis to facilitate use in the computer, is as follows:
assuming the boundary conditions,

$$T(0) = T_0 ; T(L) = T_L$$

and defining a dimensionless temperature as,

$$\theta = \frac{T(x) - T_0}{T_L - T_0}$$

where $T(x)$ = the temperature at some point (x) along the sample between 0 and L , such that,

$$\theta(0) = 0 ; \theta(L) = 1 ;$$

and letting

$$x = x_1 / L,$$

then

$$\frac{d^2 \theta}{dx^2} + \frac{J \tau L}{k} \frac{d\theta}{dx} + \frac{J^2 L^2}{k \sigma (T_L - T_0)} = 0 \quad (2B)$$

Letting

$$a = I \tau L / k$$

and

$$b = I^2 L^2 / k \sigma (T_L - T_0)$$

Equation (2B) becomes:

$$\frac{d^2\theta}{dx^2} + a \frac{d\theta}{dx} + b = 0$$

Let $\theta = \theta_h + \theta_p$ where θ_h is the solution to the homogeneous equation:

$$\frac{d^2\theta_h}{dx^2} + a \frac{d\theta_h}{dx} = 0$$

let

$$\frac{d\theta_h}{dx} = p \quad \text{then,} \quad \frac{dp}{dx} = -ap$$

$$\int \frac{dp}{p} = - \int a dx$$

$$p = C_0 e^{-ax} \quad C_0 = \text{integration constant}$$

$$\frac{d\theta_h}{dx} = C_0 e^{-ax}$$

$$\theta_h = \frac{C_0}{-a} e^{-ax} + C_1$$

θ_p is a particular solution given by

$$\theta_p(x) = -\frac{b}{a} x$$

$$\theta = -\frac{C_0}{a} e^{-ax} - \frac{b}{a} x + C_1$$

$$\theta(0) = 0 = -\frac{C_0}{a} e^{-a(0)} + C_1 \therefore C_1 = \frac{C_0}{a}$$

$$\theta = -\frac{C_0}{a} e^{-ax} - \frac{b}{a} x + \frac{C_0}{a} = \frac{C_0}{a} (1 - e^{-ax}) - \frac{b}{a} x$$

$$\theta(1) = 1 = \frac{C_0}{a} (1 - e^{-a}) - \frac{b}{a}$$

$$C_0 = \frac{a+b}{(1 - e^{-a})}$$

$$\theta(x) = \frac{(a+b)}{a} \cdot \frac{(1 - e^{-ax})}{(1 - e^{-a})} - \frac{b}{a} x \quad (3B)$$

For current flow in the reverse direction:

$$\frac{d^2 \theta_R}{dx^2} - a \frac{d\theta_R}{dx} + b = 0$$

therefore, to solve the reversal current flow problem, substitute

$a = -a$, and

$$\theta_R(x) = -\frac{(b-a)}{a} \cdot \frac{(1 - e^{ax})}{(1 - e^a)} + \frac{b}{a} x \quad (4B)$$

Equations (36) and (46) are the general solutions to the equation governing longitudinal heat flow in the rod. Calculations, using the previous equations, of position versus temperature over a linear base are shown in Figure 13. The same equations predict the slope to change in the sample as shown in Figure 14.

It is interesting to consider the change in equilibrium temperature at the middle of the rod when the current is reversed.

$$\theta - \theta_R = \Delta\theta = \frac{a+b}{a} \cdot \frac{(1 - e^{-a/2})}{(1 - e^{-a})} + \frac{(a-b)}{a} \cdot \frac{(-1 + e^{a/2})}{(1 - e^a)} - \frac{b}{a} \quad (5B)$$

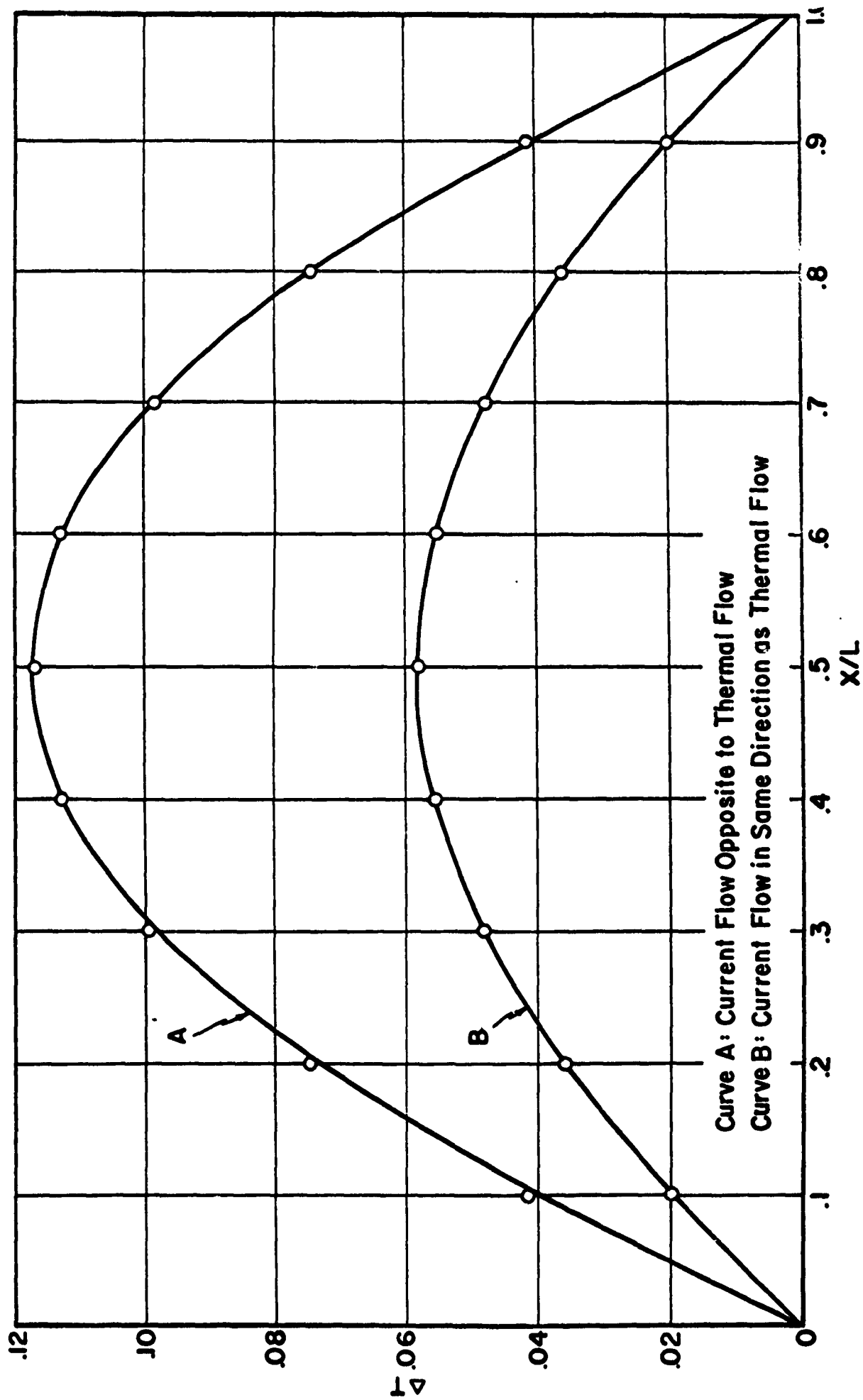


FIGURE 13 - Temperature distribution over a linear base on a nickel rod

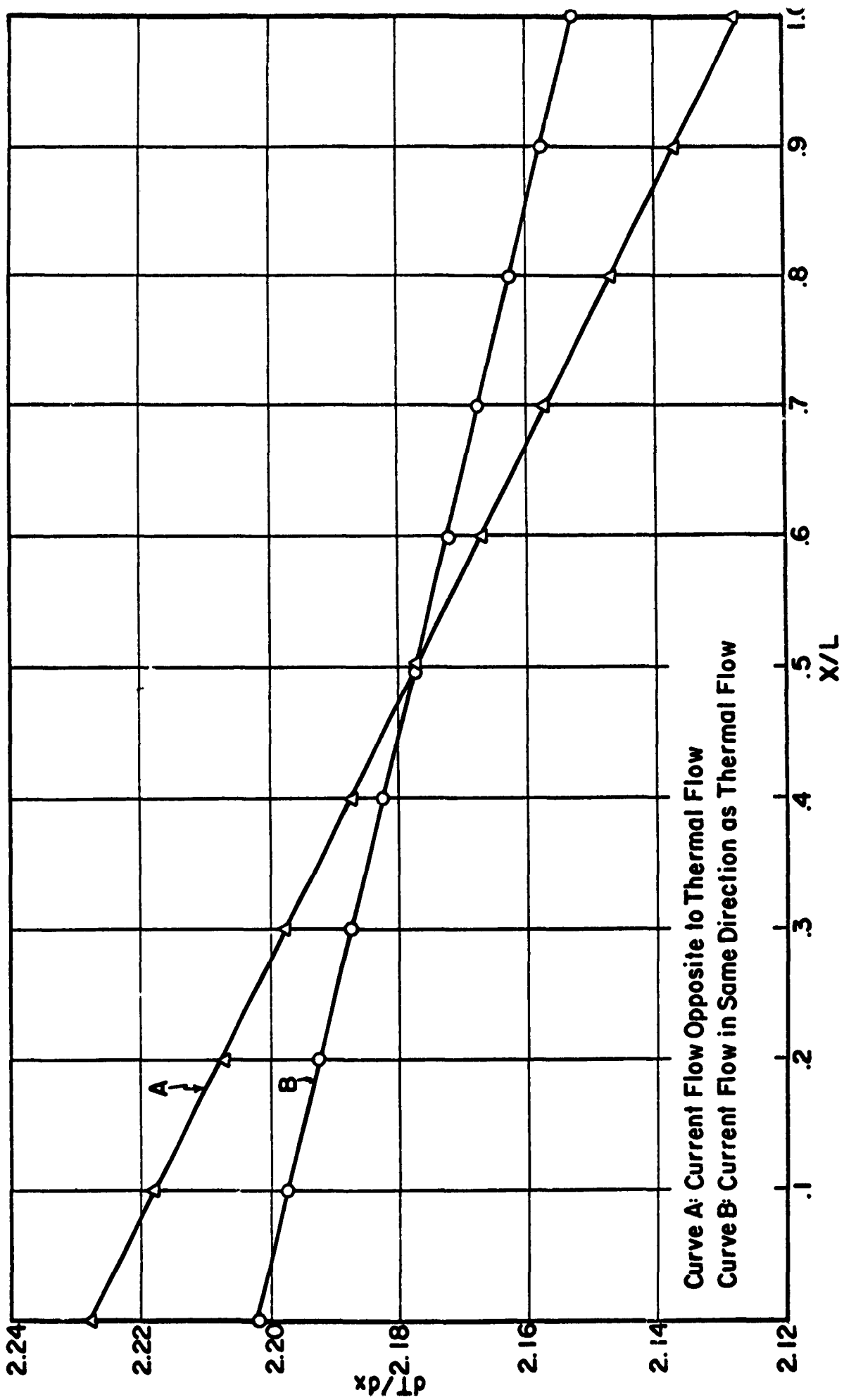


FIGURE 14 - Change in slope with position in a nickel rod

$$\begin{aligned}
&= \frac{(1-e^{-a/2})}{(1-e^{-a})} + \frac{b}{a} \frac{(1-e^{-a/2})}{(1-e^{-a})} + \frac{(e^{a/2}-1)}{(1-e^a)} \\
&\quad - \frac{b}{a} \frac{(e^{a/2}-1)}{(1-e^a)} - \frac{b}{a} \\
&= \frac{(1-e^{-a/2})}{(1-e^{-a})} + \frac{(e^{a/2}-1)}{(1-e^a)} \\
&\quad + \frac{b}{a} \left[\frac{(1-e^{-a/2})(-1+e^a) + (e^{a/2}-1)(-e^{-a}+1)}{(1-e^{-a})(-1+e^a)} \right] - \frac{b}{a} \\
&= \frac{(1-e^{-a/2})}{(1-e^{-a})} + \frac{(e^{a/2}-1)}{(1-e^a)} + \frac{b}{a} \left[\frac{-1Ae^{a/2}+e^{-a/2}-e^{a/2}-e^{-a/2}+e^{a/2}+e^{-a}-1}{(-1+e^a+e^{-a}-1)} \right] - \frac{b}{a} \\
&= \frac{(1-e^{-a/2})}{(1-e^{-a})} + \frac{(e^{a/2}-1)}{(1-e^a)} + \frac{b}{a} \left[\frac{-2+e^a+e^{-a}}{-2+e^a+e^{-a}} \right] - \frac{b}{a} \\
&= \frac{(1-e^{-a/2}-e^{-a/2}+e^{a/2}+e^{a/2}-1-e^{-a/2}+e^{-a})}{(1-e^a-e^{-a}+1)} \\
\Delta\theta &= \frac{2e^{a/2}-2e^{-a/2}+e^{-a}-e^a}{2-e^a-e^{-a}}
\end{aligned}$$

It should be noted that this result is independent of the parameter b , which includes the Joule heat and the electrical conductivity of the material.

A series expansion of the previous exponentials gives a very simple expression for Equation (5B).

Expressing

$$e^a = \sum_{n=0}^{\infty} \frac{a^n}{n!} = \sum_{n=0}^{\infty} \frac{a^{2n}}{(2n)!} + \sum_{n=0}^{\infty} \frac{a^{2n+1}}{(2n+1)!}$$

and

$$e^{-a} = \sum_{n=0}^{\infty} \frac{a^{2n}}{(2n)!} - \sum_{n=0}^{\infty} \frac{a^{2n+1}}{(2n+1)!}$$

and similarly for $e^{-a/2}$ and $e^{a/2}$. Substituting in Equation (5B) and simplifying

$$\Delta\theta = \frac{\sum_{n=1}^{\infty} \left(1 - \frac{1}{2^{2n}}\right) \frac{a^{2n+1}}{(2n+1)!}}{\sum_{n=1}^{\infty} \frac{a^{2n}}{2n!}}$$

Using the first two terms of each series yields:

$$\Delta\theta = \frac{\frac{3}{4} \frac{a^3}{6} + \frac{15}{16} \frac{a^5}{150}}{\frac{a^2}{2} + \frac{a^4}{24}} = \frac{a}{4} \left(\frac{1 + \frac{a^2}{16}}{1 + \frac{a^2}{12}} \right)$$

$$\Delta\theta = 0.99999 \times \frac{a}{4}$$

$$\Delta\theta = \frac{a}{4}$$

or

$$\frac{T(x) - T(x_2)}{T_L - T_O} = \frac{a}{4}$$

$$\Delta T = (T_L - T_O) \frac{a}{4}$$

$$\Delta T = (T_L - T_O) \frac{I \tau L}{4k}$$

$$\tau = \frac{4k\Delta T}{(T_L - T_O)JL}$$

APPENDIX C

List of Symbols

V	=	Seebeck potential, volume
π	=	Peltier heat
τ	=	Thomson coefficient
T	=	temperature
T^*	=	maximum temperature
T_{Sa}	=	temperature of sample
T_{Su}	=	temperature of surroundings
T_C	=	temperature at end of sample
T_L	=	temperature at opposite end of sample
$T(x)$	=	temperature at intermediate point in sample
θ	=	dimensionless temperature = $\frac{T(x) - T(0)}{T(L) - T(0)}$
t	=	time
S	=	thermoelectric power, entropy
S_D	=	entropy density
J^S	=	entropy flow
S^*	=	transport entropy per particle
Q^*	=	transport heat per particle
c_g	=	lattice specific heat
c_{el}	=	electronic specific heat
α	=	probability of phonon-electron collision
β	=	number of conduction electrons per atom

e	=	charge on electron, logarithmic base
A	=	cross section
$A(E)$	=	energy dependent scattering cross section
l	=	mean free path
E	=	electron energy
ϵ_0^*	=	energy of electron at Fermi surface at 0°K
J_i	=	electric and heat current flow vectors
X_i	=	forces giving rise to current flows
L_{ij}	=	phenomenological coefficients
J_e	=	particle current density
J_s	=	entropy flow density
$M_{eq}^{L_{es}}$	=	interaction coefficients
μ	=	chemical potential
$\bar{\mu}$	=	electrochemical potential
I	=	electrical current
J	=	electrical current density
ρ	=	resistivity
R	=	resistance
σ	=	electrical conductivity
k	=	thermal conductivity, Boltzmann constant
$v_{x,y,z}$	=	velocity of electrons in specific direction
f	=	distribution function
h	=	Plank's constant, heat transfer coefficient

N	=	electron density
g	=	Fermi energy per electron per electron charge
\dot{Q}_I	=	rate of heat input
\dot{Q}_A	=	rate of heat accumulated by sample
\dot{Q}_L	=	rate of heat leaving a unit volume
ϕ	=	electrical potential
c	=	specific heat
L	=	length of sample

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